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PROPOSITION D'UN PROJET DE RECHERCHE POUR ANALYSEUR PORTATIF DE MÉTAUX EN SOUTERRAIN

ANDRÉ BOYER

RAPPORT DIVISIONNEL MRL 89-142(TR)

This document is an unedited internal report prepared primarily for discussion and internal reporting purposes. It does not represent a final expression of the opinion of the Canada Centre for Mineral and Energy Technology (CANMET)

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185pp

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PROPOSITION D'UN PROJET DE RECHERCHE POUR ANALYSEUR PORTATIF DE MÉTAUX DE CHANTIERS MINIERS EN SOUTERRAIN

ANDRÉ BOYER

LABORATOIRE CANADIEN DE TECHNOLOGIE MINIÈRE

DÉCEMBRE 1989

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LABORATOIRES DE RECHERCHE MINIÈRE
RAPPORT DIVISIONNEL MRL 89-142(TR)

PROPOSITION D'UN PROJET DE RECHERCHE POUR ANALYSEUR PORTATIF DE MÉTAUX DE CHANTIERS MINIERS EN SOUTERRAIN

(Pour l'assistance journalière du géologue minier ou de l'ingénieur minier)

par

André Boyer*

RÉSUMÉ

L'objectif de ce projet de recherche est de permettre aux géologues/ingénieurs miniers d'accomplir un meilieur contrôle de la teneur en leur fournissant des appareils capable de mieux définir la minéralisation en or dans les gisements filoniens.

Étant donné l'état actuel de la recherche dans ce domaine, les travaux de recherche complémentaires devraient être concentrés sur un appareil à fluorescence X capable de détecter 1 ppm d'or et plus. De plus, il faudrait une étude détaillée des autres avenues de recherche des techniques qui semblent prometteuses reliées à l'analyse directe et indirecte de métaux. Parallèlement, il faudra entreprendre une étude sur les possibilités de méthodes indirectes impliquant l'analyse d'éléments chimiques associés à l'or qui, combinée par exemple à des mesures d'appareils géophysiques existants, permettrait de mieux définir la minéralisation en place.

Il est certain que l'utilisation de tels appareils permettrait d'optimiser l'extraction du minerai en réduisant la dilution et ainsi, réduire la quantité de matériel stérile passant au moulin. De plus, ceci aurait un impact important sur l'environnement en diminuant sensiblement le tonnage des amas de résidus miniers. Également, les renseignements obtenus grâce à ces appareils permettraient de minimiser les coûts de développement d'entailles latérales et ainsi réduire les risques d'affaiblissement des parois et toit rocheux.

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** Mots clés: CANMET/LRM, R&D, instrumentation, teneur de métaux vils et précieux, gisements d'or filoniens, ententes fédérales-provinciales.

A PROPOSAL FOR A RESEARCH PROJECT TO DEVELOP A PORTABLE METAL ANALYSER FOR UNDERGROUND MINES

(for daily support of engineers in underground mines)

par

André Boyer*

ABSTRACT

The main objective of this research project is to provide mining geologists/engineers with instruments that can define economic gold mineralisation efficiently and at low cost.

With the current status of pertinent technology, research work should be focused partly on the development of portable X-ray fluorescence instrument with a detection capability of 1 ppm of gold and over. Other direct and indirect techniques to assess in place gold mineralization such as light reflectance radiometry, that can possibly be used in metal grade analysis in combination with chemical analysis of elements associated with gold mineralization, and other geophysical instrumentation and measurement.

Such instrumentation and methods have the potential to optimize ore extraction by reducing mining dilution and decreasing the tonnage of waste material fed to the mill. Also, their use will have an important environmental impact by reducing the amount of mine tailings on surface. The additional information provided by such instruments will also minimize mine development costs.

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* Physical Scientist, Mining Research Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa.

** Key word: CANMET/MRL, R&D, instrumentation, base metal/precious metal grade, vein type deposit, federal-provincial agreements.

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INTRODUCTION

Une des tâches importantes du géologue et de l'ingénieur miniers consiste à estimer la teneur à partir de forages souterrains et d'ouvertures souterraines pour la définition de la minéralisation dans le voisinage de nouveaux développements et ainsi orienter les développements souterrains. Ces travaux impliquent normalement l'échantillonnage en vrac des épontes du site pour l'analyse de la teneur. Les résultats d'analyse arrivent au moins un jour après l'échantillonnage. Ceux-ci ne sont donc pas utiles dans le cas ou une décision doit être prise sur le champ pour l'avancement des travaux souterrains.

Pour supporter d'une façon plus efficace le géologue/l'ingénieur dans cette prise de décision, une innovation majeure serait d'utiliser un analyseur portatif de la teneur du métal économique exploité. Dans le cas qui nous intéresse, c'est la teneur en or des gisements filoniens. L'objectif principal de recherche est la version 'scanner' et l'équivalent sonde (pour les trous de sondage) d'un tel appareil qui permettraient d'obtenir des résultats instantanés sur le site.

Une investigation sur les instruments actuellement disponibles a été entreprise par le personnel des Laboratoires de recherche minière. Suite à cette recherche, quelques instruments portatifs d'analyse directe des métaux impliquant la fluorescence X ont été identifié. Ces appareils sont sur le marché depuis 1986. Cependant, dans le cas de l'or, le niveau de détection pour ce genre d'instrument est de 1 once/tonne, soit environ 30 ppm d'or, alors que pour les gisements d'or filoniens présentement exploités il faudrait analyser les teneurs de l'ordre de 1 ppm. Dans le cas des métaux vils, le niveau de détection se situe, par exemple à 0.1% et plus pour le cuivre et le plomb, ce qui est nettement satisfaisant dans ce cas.

Suite à notre investigation préliminaire sur ces technologies, une tentative de plan de recherche est décrit dans ce texte avec comme objectif initial de faire une évaluation des avenues de recherche possibles, de définir la plus plausible pour un développement subséquent d'appareil et d'estimer le coût d'un tel développement.

TOUR D'HORIZON

1) Analyseurs portatifs

Quelques analyseurs portatifs sont apparus sur le marché depuis quelques années. Ces appareils permettent à l'opérateur des mesures directes simples et sur place des éléments à quantifier. Parmi les types d'analyseurs énumérés ci-dessous, seulement l'analyseur à fluorescence-X permet d'obtenir une teneur de métal avec un niveau de détection et fiabilité/reproductibilité satisfaisants pour les métaux vils. Les diverses techniques utilisées sont:

Infrarouge

Ultraviolet/visible

Chromatographie en phase gazeuse

Electrochimie (coulométrie)

Fluorescence-X

Les critères suivants devraient être utilisés lors de la sélection d'un analyseur portatif:

a) un entretien facile et rapide de l'appareil et une vie utile suffisamment longue,

b) la reproductibilité des mesures,

c) la facilité d'utilisation, fiabilité de l'appareil et degré de compacité,

d) rapport utilité vs coût.

Pour ce qui est des métaux précieux et surtout pour les teneurs en or de l'ordre de 1 ppm, le problème est particulier et sera discuté dans le chapitre suivant.

Toutefois, relatons les efforts entrepris dans le domaine de l'analyse des métaux contenus dans la roche au Canada et ailleurs au cours des dernières années. Il faut surtout retenir les analyseurs nucléaires, tels que celui impliquant l'activation aux neutrons. La compagnie Scintrex de Toronto a déjà développé et expérimenté ce type d'appareil. Les travaux de terrain ont été exécutés sur des gisements latéritiques de la République Dominicaine comprenant des tests sur le nickel et le cuivre. Selon leur expérience dans le domaine, cette méthode n'est pas celle qu'on devrait appliquer aux

faibles teneurs en or à cause de la dimension de la matrice (détection sur un diamètre de 2.5 cm). En 1976, l'École Polytechnique de Montréal, en collaboration avec Inax d'Ottawa, a développé un appareil portatif avec une source de gaz iodé. Selon Guy Perreault (communication verbale), de bons résultats ont été obtenus pour le cuivre, le molybdène et le niobium sur des mesures faites en surface et en souterrain. Il suggère la technique de l'activation aux neutrons qui, selon lui, est la seule avenue de recherche pouvant solutionner le cas présent. Cependant, ces types d'appareils ne sont pas portatifs et sont compliqués. Selon notre opinion, ils ne devraient pas être considérés dans les projets immédiats de travaux de recherche, à moins qu'il n'y ait pas d'autres choix.

Le spectromètre de masse est un autre appareil capable d'analyser des teneurs en or de l'ordre de 1 ppm. Cependant, ce dernier n'est pas portatif et rien ne permet d'espérer qu'il le devienne dans un proche avenir à cause de la présence de la chambre de vaporisation (de l'échantillon) à haute température nécessaire pour cette technique.

Pour compléter la discussion, soulignons l'existence des appareils qui peuvent détecter la présence de certain métaux ou minéraux, tels que les appareils électromagnétiques ou magnétiques pour la détection de matériel ferreux ou, du moins, de zones minéralisées. Aussi, on peut ajouter les appareils employant soit le principe de la conductivité électrique des sulphures et du graphite (ex: méthode de mise-à-la-masse), soit celui de la suceptibilité magnétique. Il y a aussi le radiomètre à réflectance (voir Annexe-D) de Barringer Research qui est portatif et permet l'identification de certains minéraux associés avec, par example, l'or d'un gisement. Tous ces appareils sont reliés à des méthodes indirectes d'analyse de métaux et ne permettent pas de mesures directes de la teneur.

2) Analyseurs portatifs pour la teneur en or

Ces appareils sont aptes à prendre les mesures sur le site et sont facilement transportable par l'utilisateur dans un environnement souterrain.

Voici les résultats de nos recherches sur les appareils disponibles sur le marché. Les appareils identifiés sont énumérés dans le tableau suivant:

Compagnie	Nom de l'appareil	Type d'appareil	technologie
Scitec Corporation	MAP-3 analyseur portatif	'Ambient Scanner' 230	Fluorescence-X
Scitec Corporation	MAP-3 analyseur portatif	'Ambient Probe 130'	Fluorescence-X
Outokumpu Electronics	X-MET analyseur portatif	'Scanner'	Fluorescence-X
—	—	radiographe	réflectance-spectométrie

La description détaillée des appareils de Scitec et d'Outokumpu se trouve à l'Annexe-A de ce rapport. Les appareils du type fluorescence-X peuvent détecter entre 30 et 9,000 ppm d'or. Le radiographe industriel (Angleterre) est le seul appareil capable, actuellement, de détecter 1ppm d'or.

3) Analyseurs compacts, transportables

Ces appareils sont facilement transportable pour être installés dans un endroit approprié en souterrain mais ne peuvent être utilisés pour des mesures sur le site comme dans le cas des appareils portatifs. Ces appareils peuvent aussi servir à l'analyse d'éléments chimiques associés à l'or.

Compagnie	Nom de l'appareil	Type d'appareil	technologie
Seiko Instruments Inc.	Seiko I	Element Monitor	Fluorescence-X, Spectrométrie à énergie dispersive
Intermetrix Systems Inc. (BRGM)	Syrano 3		Fluorescence-X, Spectrométrie à énergie dispersive

La description détaillée de ces appareils se trouve à l'annexe - B avec quelques textes sur la théorie et les concepts reliés aux corrections pour compenser l'effet de matrice.

Ces appareils utilisent la fluorescence à rayons-X avec la spectrométrie à énergie dispersive produit par un courant électrique. Il sont transportables et doivent être installés à un endroit approprié, protégé de l'humidité.

Il serait possible de distinguer l'or à partir de 3 ppm dans certains cas. L'analyse se fait sur des échantillons réduits en poudre et demande donc une étape intermédiaire d'échantillonnage-broyage.

LA PROBLÉMATIQUE

Comme nous l'avons spécifié au début du rapport, les appareils portatifs à fluorescences-X sont présentement capables de détecter des concentrations d'or d'environ 30 ppm d'or ou plus. D'après notre information, le seul instrument capable de détecter 1ppm d'or est l'appareil impliquant la radiographie industrielle, (communication verbale avec Lloyd Dalton, LSM) développé en Angleterre pour les gisements d'or d'Afrique du Sud. Cependant, l'appareil coûte environ $600,000.00, ce qui le rend pratiquement inabordable pour la plupart des opérations minières canadiennes existantes.

Le point critique qui empêche la détection des teneurs d'or de l'ordre de 1 ppm avec la technique de la fluorescence-X (portatif avec isotope radioactif) est l'effet de matrice surtout pour d'aussi faibles teneurs. La réponse à l'excitation électronique est mille fois plus grande de la part des éléments associés à l'or. Et surtout, les profils

montrant l'énergie libérée par ces divers éléments font interférence à ceux de l'or et ne permettent pratiquement pas les mesures de teneurs en or pour les quantités inférieurs à 152 ppm d'or, quel que soit le degré de sophistication de l'appareil. Le niveau de détection et de quantification de l'or pour des teneurs inférieures à 152 ppm est possible avec la technique de fluorescence-X de la spectrométrie à énergie dispersive à cause de la quantité d'énergie plus grande utilisée dans le second cas.

Le prix des appareils à fluorscence-X portatifs ou transportables varie entre $35,000.00 et $75,000.00.

Lloyd Dalton des Laboratoires de sciences minérales de CANMET est présentement impliqué dans un projet de recherche sur un appareil à fluorescence-X (voir Annexe-C). La première phase du projet vise à vérifier s'il est possible de détecter 20 ppm d'or en employant un certain type d'isotope radioactif. La couche d'électrons K est celle considérée dans ce cas. Si la première étape s'avère un succès, la seconde consiste à faire l'analyse statistique de 200 échantillons pour vérifier la fiabilité des résultats. Selon Lloyd Dalton, aucun autre projet n'est prévu, du moins pour le moment, pour la détection de l'or à un niveau inférieur à 20 ppm.

Une avenue prometteuse de recherche serait la technologie impliquant le détecteur au germanium pur pour l'analyse de rayons gamma provenant de l'or radioactif. L'appareil portatif résultant serait à la fois un appareil à fluorescence-X en plus d'être un mini réacteur atomique. Cette technologie permettrait de faire l'analyse de teneurs en or plus faibles que celles possibles par la fluorescence-X à énergie dispersive.

Une autre avenue de recherche pour le développement d'un analyseur capable de détecter 1 ppm d'or est celui appliquant l'activation aux neutrons. Comme décrit plus tôt dans le texte, cette approche est plus compliquée que la précédente et demande un budget de recherche plus élevé. Il ne semble pas y avoir, présentement, de développement dans ce domaine au Canada.

Dans le domaine des appareils transportables, il faudrait vérifier la technologie impliquant le spectromètre à arc pour l'analyse d'échantillons d'or réduis en poudre par broyage ou fragmenté dans un liquide par ultra-sons. Cette approche implique également le développement d'une méthode d'échantillonnage en souterrain par trous de forage ou autres.

Actuellement, l'analyse des teneurs en or de l'ordre du ppm avec un instrument portatif (à prix abordable pour le client) demeure un point d'interrogation.

Il faudra considérer, aussi, la possibilité d'utiliser les méthodes chimique traditionnelles (humides) et le développement d'une trousse portative pouvant être utilisée en souterrain. Le temps nécessaire pour la préparation de l'échantillon, la mise en solution et la concentration de l'élément, par exemple l'or, devrait être assez court, soit moins de trente minutes.

Note: Il est surprenant de constater que les instruments de géophysique du type sonde (pour les trous de sondage) ainsi que les analyseurs portatifs de métaux du type 'scanner' ou sonde ne sont pas intégrés à la pratique courante du contrôle de la teneur dans le cas des exploitations minières pour les métaux vils. Les principaux aspects à considérer sur la question sont:

Rapport coût/bénéfice; est-ce nécessaire?

Connait-on l'existence de ces appareils?

Est-ce dû à l'attitude neutre, conservatrice?

OBJECTIFS

Tel que mentionné au début du rapport, l'objectif principal du projet consiste à développer un analyseur de métaux et plus spécifiquement un analyseur pour l'or. Cet appareil doit être portatif et d'utilisation simple pour les mesures en place à effectuer en souterrain. Deux versions ('scanner' et sonde) de cet appareil devront être développées pour permettre une meilleure définition en 3-D de la minéralisation en or d'un site à exploiter.

Si les méthodes directes s'avèrent impossibles dans l'état actuel des connaissances, il reste à explorer le domaine des méthodes indirectes ou semi-quantitatives. De telles méthodes permettraient aussi une meilleure définition de la minéralisation sans, toutefois, mesurer la teneur en or de la masse rocheuse.

Selon les budgets disponibles, une autre option serait de mener parallèlement les deux projets: méthodes directes et indirectes.

PLAN DE RECHERCHE

PHASE I: Méthodes directes

Evaluer la teneur en or de 1 ppm et plus en utilisant d'abord la technologie impliquant la fluorescence-X. Si cette première possibilité s'avère impossible nous devrons faire le même exercice avec la technologie impliquant l'activation aux neutrons. Dans les deux cas, il s'agit de développer un appareil portatif à prix abordable, fiable et surtout pratique pour l'utilisateur dans un environnement souterrain.

Stratégie

Un montant initial (à être fixé) devra servir à évaluer les avenues possibles. Pour cette étape, le contracteur devra fournir un personnel avec plusieurs années d'expérience dans les mesures de radiations ainsi que dans l'assemblage de sources d'excitation nucléaire.

Suite à cette évaluation, si une avenue de recherche est jugée prometteuse, nous poursuivrons avec les travaux de laboratoire. Sinon, la phase I sera arrêtée et le projet se poursuivra avec la phase II.

Les étapes à respecter sont les suivantes:

PHASE I-A (ÉVALUATION)

1. Si nécessaire, obtenir la permission du Contrôle de l'Énergie Atomique du Canada pour l'utilisation de matériaux radioactifs, c'est-à-dire la quantité nécessaire de l'isotope désigné pour les travaux;

2. En conjonction avec le chargé de projet, évaluer l'approche ([1]) technique qui pemettra l'analyse des teneurs en or de l'ordre d'un ppm. Le critère de sélection du contracteur est celui d'éviter des conflits d'intérêts personnels. Le contracteur retenu doit faire appel à des spécialistes de chaque domaine technique ou principe évalués.

PHASE I-B (DÉVELOPPEMENT)

Suite aux résultats de la PHASE I-A nous serons en mesure de juger si l'on doit ou non continuer les travaux. Si l'évaluation est favorable, les étapes suivantes seront possibles:

3. Conception et assemblage de l'appareil par le contracteur (ce dernier peut être différent de celui de l'évaluation) en utilisant, si possible, les installations disponibles (voir les conditions plus loin).

([1]) Comme étape préliminaire, faire la planification et l'exécution des travaux pour l'essai en souterrain des appareils à fluorescence-X existants. Ces travaux peuvent être entrepris par le personnel des Laboratoires de recherche minière d'Ottawa.

4. Expérimentation de l'appareil en souterrain dans des opérations minières sélectionnées par le chargé de projet. Cette étape comprendra aussi l'analyse statistique des mesures pour vérifier la fiabilité de l'appareil.

5. La préparation d'un rapport sur l'analyse des données et évaluation de l'appareil, incluant une discussion sur les cas étudiés.

6. Si le projet s'avère un succès, en conjonction avec les ententes préalablement faites avec la Division du Marketing de la technologie et le chargé de projet, il faudra finaliser les procédures pour obtenir brevet et license avant la mise en marché de l'appareil.

Conditions

Afin de minimiser les coûts, il serait préférable, si possible, que le laboratoire du contracteur soit équipé avec l'instrumentation nécessaire pour mesurer, par exemple les radiations, ainsi que tout autre équipement de base devant servir au projet.

PHASE II: Méthodes indirectes (optionnelle)

Comme pour la PHASE I, les mêmes critères d'appareil doivent être respectés, c'est-à-dire: un appareil portatif, de manipulation assez simple donnant des résulats fiables, reproductibles, avec un bon rapport coût/utilité.

Les étapes suivantes devront être respectées:

PHASE II

1. Évaluation de la technologie disponible, adéquate ou adaptable à l'analyse semi-quantitative ou autre des gisements d'or filoniens, pour permettre une meilleure définition de la minéralisation. Le critère de sélection du contracteur est celui d'éviter des conflits d'intérêts personnels. Le contracteur retenu doit faire appel à des spécialistes de chaque domaine technique ou principe évalués.

2. Le contracteur retenu lors de l'évaluation doit être capable d'adapter une méthode en développant, par exemple, des algorithmes pour l'appareil sélectionné. Développer pour l'appareil en question une procédure d'utilisation en expérimentant l'appareil dans des sites d'exploitation minière souterraine choisis par le chargé de projet.

3. Préparation d'un manuel de l'usager.

(Note: Plusieurs appareils peuvent faire parti du projet impliquant soit le même contracteur ou différents contracteurs.)

BÉNÉFICES ANTICIPÉS

Si les objectifs de la phase I et/ou de la phase II sont atteints, les bénéfices sont:

a) Acquérir une meilleure connaissance des limites de la minéralisation d'un gisement au stade d'exploitation, par des mesures appropriées faites sur le site même. Ceci permet d'optimiser l'extraction en réduisant la dilution et donc en diminuant la quantité de matériel stérile passant au moulin et par le fait même, la quantité de résidus miniers en surface. Ceci représente donc un impact positif important sur l'environnement.

b) Comme nous le savons, plusieurs millions de dollars sont dépensés annuellement pour des entailles latérales, afin de mieux définir les limites du minerai. Ce type d'appareil permettra de minimiser les coûts de développement de ces entailles en remplaçant ces dernières par des mesures sur des ouvertures souterraines.

c) Ce type d'appareil peut améliorer la stabilité des ouvertures en chantier, en réduisant les entailles latérales non utiles qui risquent d'ébranler les parois et le toit, créant un risque additionnel à la sécurité des mineurs.

ESTIMATION DES COÛTS

Au stage actuel du projet, le coût d'évaluation de la PHASE I-A ou II-A est estimé entre $10,000.00 et $20,000.00 pour l'évaluation seulement. Le développement d'appareils sera d'au moins un ordre de grandeur supérieur à ceux de l'évaluation.

Suite à l'évaluation (PHASE I-A ou II-A), les coûts de recherche et développement seront fixés en fonction de la difficulté du projet. À ce stade du projet, il sera alors possible de prendre une décision éclairée en fonction des coûts estimés et du degré de possibilité de réussite du projet.

ANNEXE - A

INFORMATION TECHNIQUE SUR LES APPAREILS PORTATIFS À FLUORESCENCE-X UTILISANT LES ISOTOPES RADIOACTIFS

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SPECIFICATIONS & TECHNICAL INFORMATION

SUMMARY

MAP instruments use the principles of energy dispersive x-ray fluorescence spectrometry to provide ore grade information in the field, mine, lab or mill, almost instantaneously. MAP enables an operator to make numerous in-situ analyses, effectively increasing the total "sample size." This leads to more accurate grade assessment, improved decisions, less waste and higher quality of ore mined and milled.

Savings depend on specific applications. Demonstrated savings have ranged from hundreds to thousands of dollars a day. MAP can make the difference between a marginal mine and a profitable mine.

In short, MAP instruments:

(1) Make in-situ measurements
(2) display grades immediately
(3) cost less than current sampling practices
(4) lead to more accurate valuation than other methods currently in use.

SCIEN TIFIC BASIS

XRF Spectrometry

Whenever the elemental composition of a solid or liquid needs to be known or controlled, the most general and simplest analytical technique available is energy-dispersive x-ray fluorescence spectrometry (XRF). XRF is applicable whether the question involves identification of an unknown material, multielement quantitative analysis, or routine and repetitive screening of hundreds or thousands of samples. Unlike "wet" chemical analysis, XRF is based on the generation, detection and measurement of the spectrum of x-rays emitted by the sample elements under x-ray bombardment. The method is fast, requires no sample preparation, and is both nondestructive and nonconsumptive.

The power of XRF as a general analytical tool lies in its combination of elemental survey capabilities and simplicity, and the ability to "tune" the excitation source to the problem (Source-Tuned XRF). Techniques such as atomic absorption (AA) look at specific selected elements, while XRF can survey a combination of elements.

Atoms of every element emit characteristic x-rays when bombarded by high energy x-rays. An atom is "excited" or ionized when probing radiation is of sufficient energy to completely remove an electron from its normal atomic level. Total energy increases. The atom immediately "relaxes" back to its original energy state by transferring an electron from an outer electron shell to the inner shell vacancy and releasing energy.

FIGURE 1

The energy is released by the emission of an x-ray photon with an energy level "characteristic" of the element, thereby providing information on the specimen's qualitative and quantitative composition. The bombardment, electron movement and detection of energy as performed by MAP equipment are shown in Figure 1.

Electrons are arranged in concentric "shells" at increasing distances from the nucleus. These shells are labeled K, L, M, N, etc., the "K-shell" being the closest to the nucleus, the L shell next and so on.

An advantage of K-shell fluorescence is that the fluorescence energies of the K-shell in every mineral are approximately seven times stronger than those of the L shell, effectively increasing the sample size to seven times larger and deeper than L-shell XRF techniques. This larger sample volume provides more reliable and precise analysis.

In addition, the energy difference between the K-shell fluorescence of any two elements is approximately seven times greater than the L-shell energy difference. This provides accurate discrimination between metals and minimizes interferences.

In the past, XRF has been used to measure concentrations of molybdenum, antimony, tin, lead, tungsten and the rare earths. Now, with the recently developed cryogenic systems with ultra high speed count rates, gold, platinum and mercury can also be detected.

Characteristic x-ray production from a particular element is most efficient when the excitation energy of the x-ray source used is just above the minimum level or "edge" of that element. The ideal excitation is a source of x-rays

having an energy just above the critical absorption edge energies of the target elements of interest.

Some radiation emitted by an element can be absorbed by another element in the same sample, which in its turn emits radiation. This phenomenon can lead to overestimation of the second element to the detriment of the first. These matrix effects and interferences can be corrected by a computer program which takes into consideration the primary and secondary elements to be determined and the matrix.

The presence of significant quantities of metal other than the target metal has the effect of "shielding" the target metal's fluorescence. This situation tends to decrease the precision of the XRF analyses. This shielding effect can be minimized by taking longer analyses or by developing a custom calibration.

Sampling Considerations

Error in measurement of ore values occurs when individual samples are used to estimate values. The value of a large mass of ore is taken as the average value of a suite of samples from the ore. Since in any ore sample the target metal's location and orientation are not predicable, any measurement made (by any means) of a small sample which is taken from a larger sample is dependent on the smaller sample being "representative" of the overall ore sampled. Absolute representation is seldom the case.

The erratic values of metal concentrations in ore necessitate the evaluation of large numbers of samples for accurate

valuation and ore reserve estimation, yet time and manpower requirements make collection of large numbers of samples uneconomical and place a limit on the frequency of sampling which is practicable.

The problem inherent in current sampling practice is that too few samples are taken to be accurately representative of a given ore body, since the time necessary to evaluate a sufficiently large number of samples is prohibitive using traditional techniques. Real time in-situ analysis provides the means for overcoming this problem by making large numbers of sample results economically available.

SYSTEM FEATURES

General Description

MAP systems consist of a "sensor" ("probe," "scanner," or "station") connected by a cable to a battery-powered microprocessor "console" packaged into a small, rugged, environmentally-sealed case for field and in-mine use (see Figure 2). The entire system can easily be carried and operated by a single person.

The MAP systems can be used in a "scanning" mode by observing the rate of flashing of a count light on the control console or by listening to an audio beeper. The scanner can be moved continually until a significant count rate occurs, at which point more detailed analyses can be made. Averaging across a given distance can also be done in a stop and go fashion, at the end of which the grade displayed will be the accumulated average of the area sampled.

Grade values are displayed visually and are stored, together with an identification number (and footage when using a probe at depth), in a protected memory. The

microprocessor can be connected to the printer to produce a record of the stored data or data can be directly downloaded to a computer.

MAP equipment is designed to withstand rough handling and severe mine environments including high moisture (even rain) and temperatures from -6C (20F) to 43C (110F). Measurements or grade values can be given in parts per million (ppm), percent by weight, ounces, or grams per ton, based on the determined amount of the target metal in the irradiated sample.

Existing sensors are designed for use on minerals between the atomic weights of #42 (molybdenum) and #92 (uranium); this includes gold, silver, platinum molybdenum, uranium, palladium, tungsten, mercury, antimony, tin and lead.

Custom systems can be designed for applications including on-line mill stream processing and control, carbon-in-leach or carbon-in-pulp systems, heap leaching control, tailings monitoring and monitoring of contaminated soils or solutions.

MAP can analyze certain elements simultaneously, and can hold up to 10 different calibrations. Actual quantitative measurements are automatically calculated and displayed in an easy to read format on an alphanumeric display.

To produce optimum results, the source must be matched to the target metals you specify.

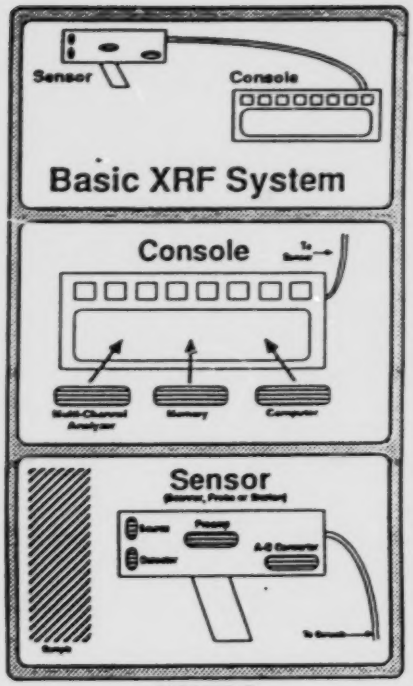


FIGURE 2

1. Americium (Am-241, useful life: 473 years) for: Silver, tin, antimony, molybdenum, palladium, barium and the rare earth metals.

2. Cobalt (Co-57, useful life: 1 year) for: Gold, uranium, tungsten, lead, platinum.

MAP's precision correlates closely to fire or wet chemistry assay results, and has proven to produce more accurate valuations than chip or channel sampling.

Specific Features

Choice of Sensors - The MAP user has a choice of sensors: downhole probe, scanner or station...calibrated with a selected radioactive source...for exploration, grade control, mill processing or laboratory use.

Reliability - Each unit undergoes high-low temperature and shock/vibration tests before delivery. MAP equipment has been used in the field for years and has performed thousands of analyses reliably, with very little downtime or loss of accuracy.

Simple Keypad Operation - All functions are controlled by keypad, performed with 1 or 2 strokes for simple, straightforward operation. Keys have positive tactile feel and are weatherproof.

Batteries - The rechargeable batteries of the microprocessor provide over ten hours of continuous use. Batteries can be changed quickly, and used batteries recharged overnight.

Cryo-cooling - The cryo units (scanner and station) use a cryogenically cooled GeLi detector. Super cooling is achieved with liquid nitrogen. The liquid nitrogen storage Dewar in the station will provide up to 24 hours of usage without refilling. The cryo scanner Dewar requires refilling about every 8 hours.

320 Character LCD Display - The large 8 line by 320 character display screen guides the operator step by step through all operations and displays ore grade information, XRF spectrums and other information.

Display of Data - Each measurement is shown on the LCD display and stored in system memory. At any time the operator can call up and review the data in memory, allowing comparison of values and maintenance of data quality. On-board memory can store more than 1000 entries, including measurement values, ID numbers, time and depth of analyses.

Information Access and Organization - Data is displayed and stored for printout or downloading to a computer. Analyses are sorted by depth (if using a probe) and number for easy reference or comparison, regardless of the sequence in which they were taken. The user-friendly software-controlled microprocessor can be easily updated for new accessories or enhancements.

Flashlight - A "count-rate" light indicates the approximate grade.

Applications Software - The control console microprocessor can be easily linked to your computer and used for mine modeling software programs.

Accuracy Control - Accuracy is a direct function of analysis time; analyses can be set to any length you desire. Preprogrammed times are set at 60 and 120 seconds. A "manual" assay mode allows you to assay from 10 seconds to several hours.

Life Expectancy - MAP systems are still in use after years of operation with minimum maintenance. Radioactive

sources used for gold, tungsten, uranium, platinum and lead require replacement at one year intervals.

Maintenance - MAP is reliable and rugged. Service and repair maintenance is available from MAP service centers.

Equipment Alarm Messages - Messages warn of mistakes such as operator entry errors or failure to follow directions.

Fail-Safe Memory - Memory is powered from an uninterruptible power source. If the main batteries are discharged or removed, the memory will still retain your data. To prevent accidental erasure, memory can be cleared only by a series of keystrokes.

Total Portability - The system is powered by rechargeable batteries that operate over 10 hours in the field. The batteries function at any attitude. The entire system is lightweight and carried easily by one person and will operate in all environments normally encountered.

Ease of Use - The large display provides menu driven operation. Scitec will train your operator in system operation, safety and sampling techniques.

Outputs to Many Peripheral Devices - The system output is a standard RS-232 serial port. All stored data can be transferred through this port to a printer or to a computer. This allows the data to be stored on disk, transferred with a modem over telephone lines to another location, or be sent to a printer.

Safety - MAP sensors utilize a small radioactive source. The dose rate from use of the scanner is significantly below the minimum levels allowed. The system, approved for sale by Washington State Department of Social and Health

Services, is safe is use providing normal precautions are followed. Radiation safety training is required prior to delivery.

Adaptability - MAP systems compensate for non-uniform surfaces, changing matrix conditions and grain size with an advanced and proprietary spectrum analysis technique. MAP analyzes minerals in all forms from solutions to solids.

Versatility - MAP is the only instrument that measures ore down drill holes, on the mine face, muck pile, waste storage, mill belt feed, in the field, concentrates or leaching towers across a wide grade range, without sample preparation.

Detection Limits - In essence, there is virtually no lower "limit" of detection with an in-situ analyzer. If a target mineral is within the sample being analyzed it will fluoresce. The amount of fluorescence that occurs depends on the amount of target metal present and the length of analysis. When extremely low concentrations (say less than 1 ppm) are in the sample, a very low amount of fluorescence occurs, providing little data to make precise measurements. If high precision is required on low concentrations a longer analysis time is required.

SYSTEM OPERATION

Console

The "control console" is the heart of every MAP system. All analyses are enacted within the console's multi-channel analyzer and microcomputer, then are displayed on the console's LCD display.

The console can operate with any one of the various "sensors" used to measure the fluorescent reactions of the minerals within the sample.

The console houses a dedicated microprocessor with memory for over 1000 analysis and a multi-channel analyzer which performs XRF spectrum analysis utilizing the MAP patented software technology.

The console's 14 key tactile feel keypad allows convenient operation. User friendly menu type software allows easy, error free operation and analysis. The console houses lightweight, rechargeable batteries.

The MAP console can be reprogrammed without sending the system to a service center by collecting sample data yourself and sending it via modem or a floppy disk to the factory. New software can be programmed within hours and installed via modem or your floppy disk.

New software updates and other new features can keep your MAP-3 console "state of the art" for years to come.

Sensors

Sensors have been designed in various configurations for every type of mining need.

The pistol style hand held "scanner" series is the most popular because of its wide flexibility. Scanners are used in reconnaissance to collect thousands of assays in days. They are used to analyze drill cuttings and placer samples on the spot to guide drilling and development work. Using a MAP scanner, core samples can be 100% analyzed without destroying any sample.

In the mine, the hand held scanner is used to channel and bench sample. Used in the "scanning mode", the hand held scanner can calculate average values over an entire face or bench. The scanner is also used to sample ore cars, draw points, muck piles, storage piles, belt feeds, concentrates and even solutions. "Ambient" (room-temperature) and "cryogenic" (super-cooled) scanners are available.

For many applications, the small, light and flexible ambient system is the most suitable alternative. Highly accurate analyses of silver, tin, molybdenum and the rare earths, along with uranium, tungsten and lead can be performed ideally with the combination of a MAP-3 console and a MAP ambient scanner.

A scanner is also available utilizing the liquid nitrogen cooled cryogenic detector system by Scitec. This pistol grip scanner is designed for high sensitivity and precision analysis of gold, platinum, silver and other metals. Combining the ease of a scanner with the highly sensitive precision of cryogenics, the MAP cryo-scanner is the only in-situ analyzer for gold and platinum available.

MAP SYSTEM OPERATION

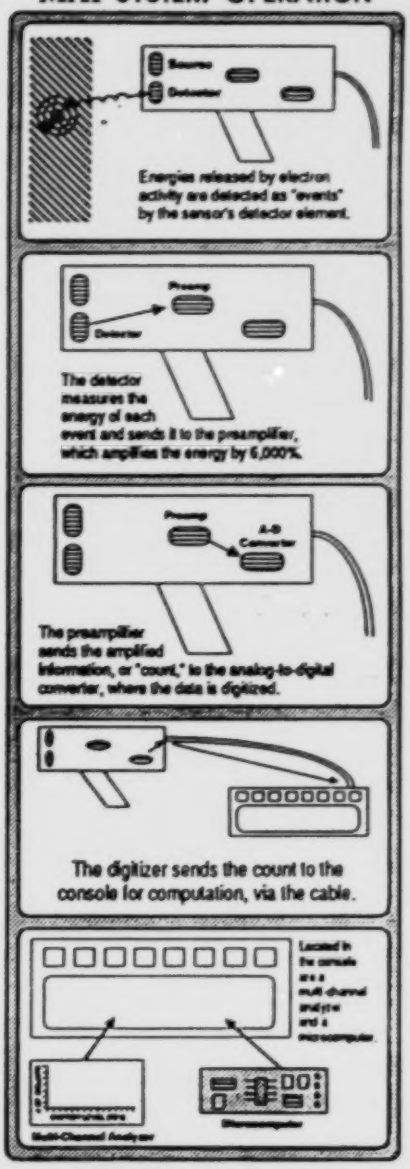


FIGURE 3 - Continues→

MAP SYSTEM OPERATION (Cont.)

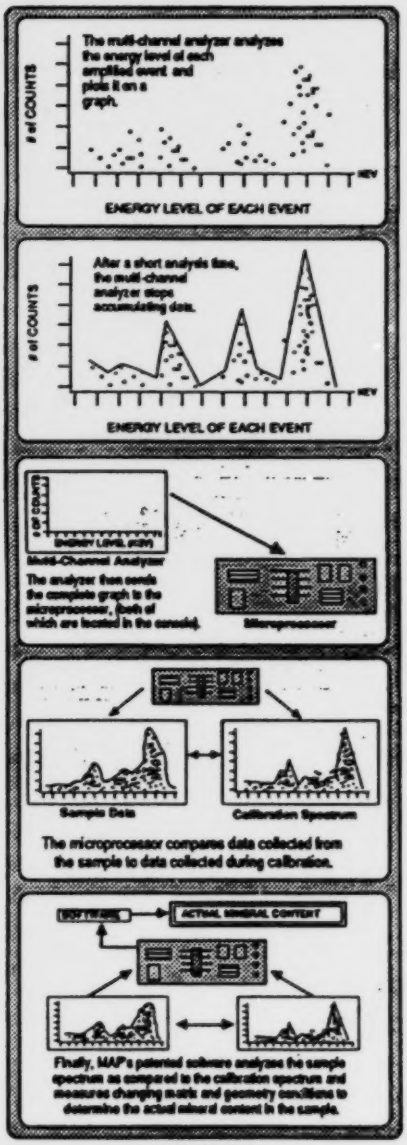


FIGURE 3

Scitec's cryogenic technology is also used in the "cryo station," a free-standing portable sensor which measures high-sensitivity metals by the insertion of samples into a chamber within the sample station.

Another sensor configuration is the "probe," a 38-inch shaft designed to perform downhole logging in almost every size hole, vertical, horizontal or angled. The probe is an ambient sensor and is water and pressure proof down to 8,000 feet. It is used in longholes, blastholes, exploration holes and test holes. Mineralized zones can be more accurately defined and drilling directed based on real time downhole information.

MAP operation is shown graphically in Figure 3.

Safety and Training

MAP Systems contain a small radioactive isotope "source" specifically selected to excite atoms within the target metals you choose. The source is encapsulated within a specially designed sealed holder so the dose rate is very small. It is safe to use with normal precautions.

Operators must be trained and licensed to operate and handle MAP. Some countries require additional safety and health licenses, import licenses or other types of registration. Scitec will assist you in securing such approvals or licenses.

MAP is safe and easy to use. No special technicians are required, operator training takes only one or two days.

Calibration

"Calibration" is the process of collecting XRF data on ore "standards" or samples of known ore value and matrix conditions. This establishes the amount of fluorescence a MAP instrument measures with a specific source and detector. This XRF data is mathematically regressed to the known assay values to develop a "best fit" line. This line will correlate to the known values better than 98% of the time.

Accuracy

The standard error of measurement with an in-situ analyzer is independent of the grade; it is instead determined by the time taken to make the measurement. This is because the precision with which the energy spectrum is defined is a direct function of the time over which the randomly emitted x-rays are collected. This in turn affects the precision with which the mineral concentration can be calculated. The relationship between standard error of measurement and the time of measurement is shown in Figure 4.

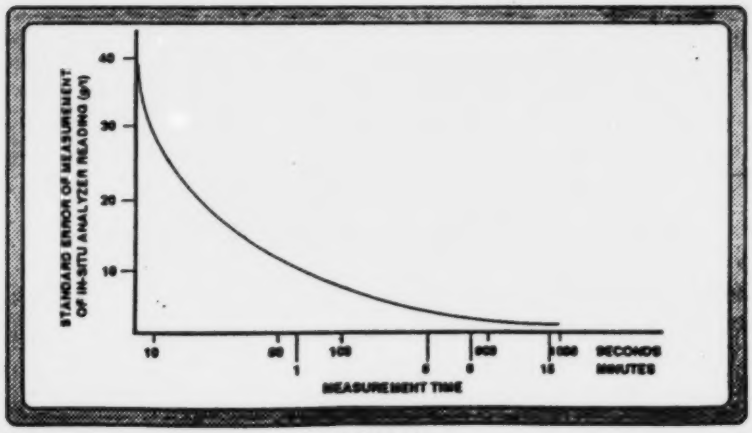
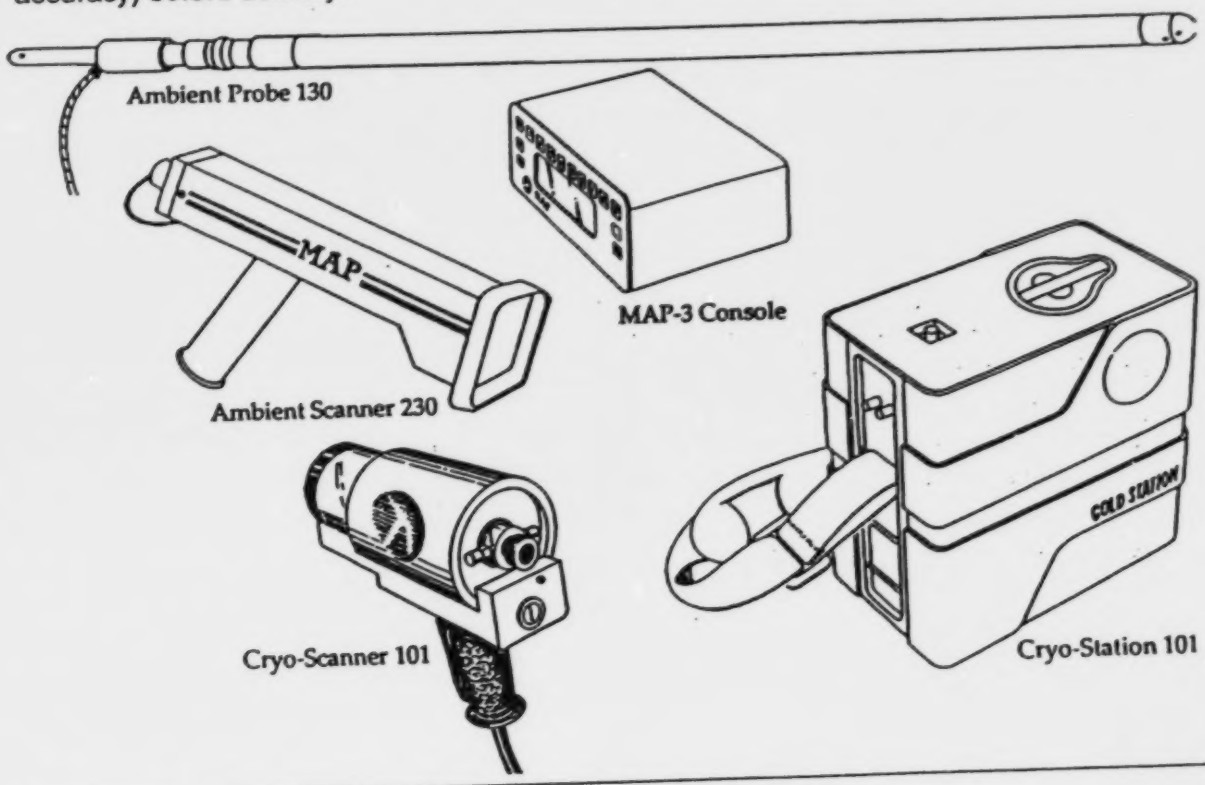


FIGURE 4

MAP™
PORTABLE ANALYZERS

Specifications

A MAP portable assay system consists of a "console" connected by a cable to a "scanner", "probe" or "station." Each system is thoroughly tested (vibration, heat and calibration accuracy) before delivery.

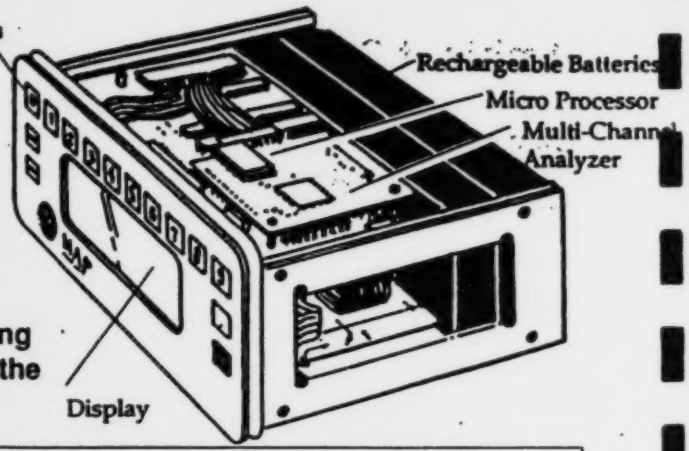


BASIC SYSTEM

Only one console is needed, and can be attached to any of the "sensors." 1) Control Console with battery power and cable 2) Your choice of "sensors"; Ambient Probe, Cryo-Station, Cryo-Scanner or Ambient Scanner 3) Spare batteries 4) Battery Charger 5) Carry Pak 6) Storage and Shipping Containers

Control Console: MAP-3

The control console is the centerpiece of the MAP Portable Assay System; it is connected to any one of the sensor options with a 6 m (20 ft) cable assembly and comes with carry pak, target metal calibration, shipping container and operating instructions. The console is composed of the following components:



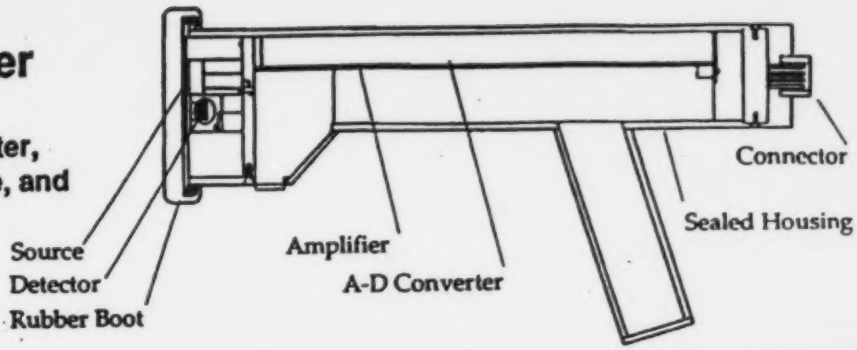
- 256 channel, miniature, field rugged, multi-channel analyzer; manufactured by Scitec Corporation.
- Dedicated microprocessor system manufactured by Scitec processes up to 1,000,000 counts per second; RS-232C interface.
- EEPROM - Electrically erasable programmable read only memory integrated circuit, allows software updates via modem or computer hookups.
- Storage capacity of 1 megabyte of information or approximately 1000 spectrums and analyses.
- 1.75 inch by 6.35 inch (4.4 cm by 16.1 cm) Supertwist LCD window displays 8 lines by 40 alphanumeric characters and 240 dot (w) by 64 dot (h) graphics.

  Readouts include:

  - Operation menu: Step by step instructions for error free operation.
  - Grade values in your choice of 3 languages; up to 6 metals at one time in ounces per ton, grams per ton, parts per million or percent by weight from 0 - six digits.
  - Up to 8 different calibrations or sample conditions.
  - Count rate digital readout shown in counts per second.
  - Analysis time clock shows measurement time remaining in seconds.
  - Analysis ID number and the number of the analyses stored in each ID area.
  - Depth of the probe in the bore hole when used in conjunction with a winch.
  - Graphic spectrum of fluorescence analysis.
- Memory: For access and hard copy printout.
  - List of analyses taken
  - Depth that each measurement was taken (when connected to the winch and probe)
  - ID number of each measurement
  - Length of time for each measurement
  - Name of element measured
- Count rate LIGHT and high pitch BEEPER denoting count rate being received and processed by the system detector.
- 14-Key Keypad: Weatherproof, positive tactile feel numeric keys.
- Power Supply: 2 Gel-Cell type 12 VDC rechargeable batteries stored in the modular battery pak for easy replacement. Each battery pak is capable of 4 - 10 hours continuous use without recharging. Each MAP system comes with 2 battery paks. Each Gel-Cell has an approximate useful life of 12-18 months or 150 recharges. Weights 1.2 kg (3 lb). Operates at any orientation at -6°C (20°F) or higher.
- Size: 19.3 cm (7.6 in) long x 20 cm (8 in) wide x 7.6 cm (3 in) high
- Weight: 4.1 kg (9 lb) with battery pak
- Power Requirements: 24 VDC, 6 watts
- Environmental: Splashproof 100% humidity, operates at any angle
- Tested: Hot and cold tested for 8 hours at temperatures between -6°C (20°F) and 43°C (110°F)
- Construction: High-impact plastic
- Connectors: 1 breech lock type, connects to battery charger and a standard RS-232 port

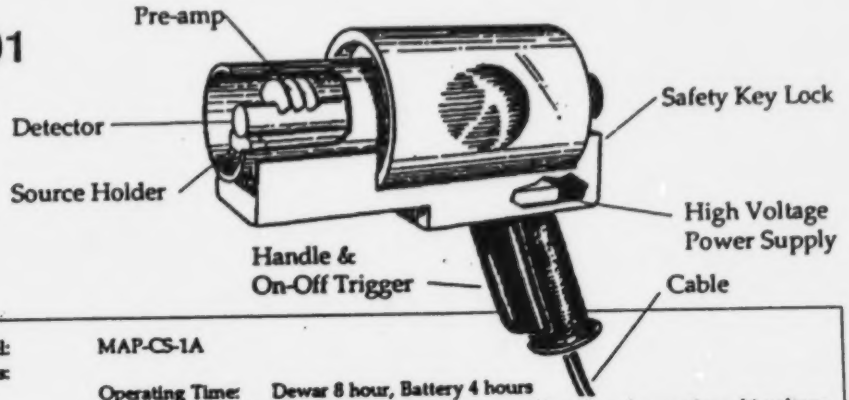
Ambient Scanner

Comes with survey meter, carry case, 6-foot cable, and operating instructions



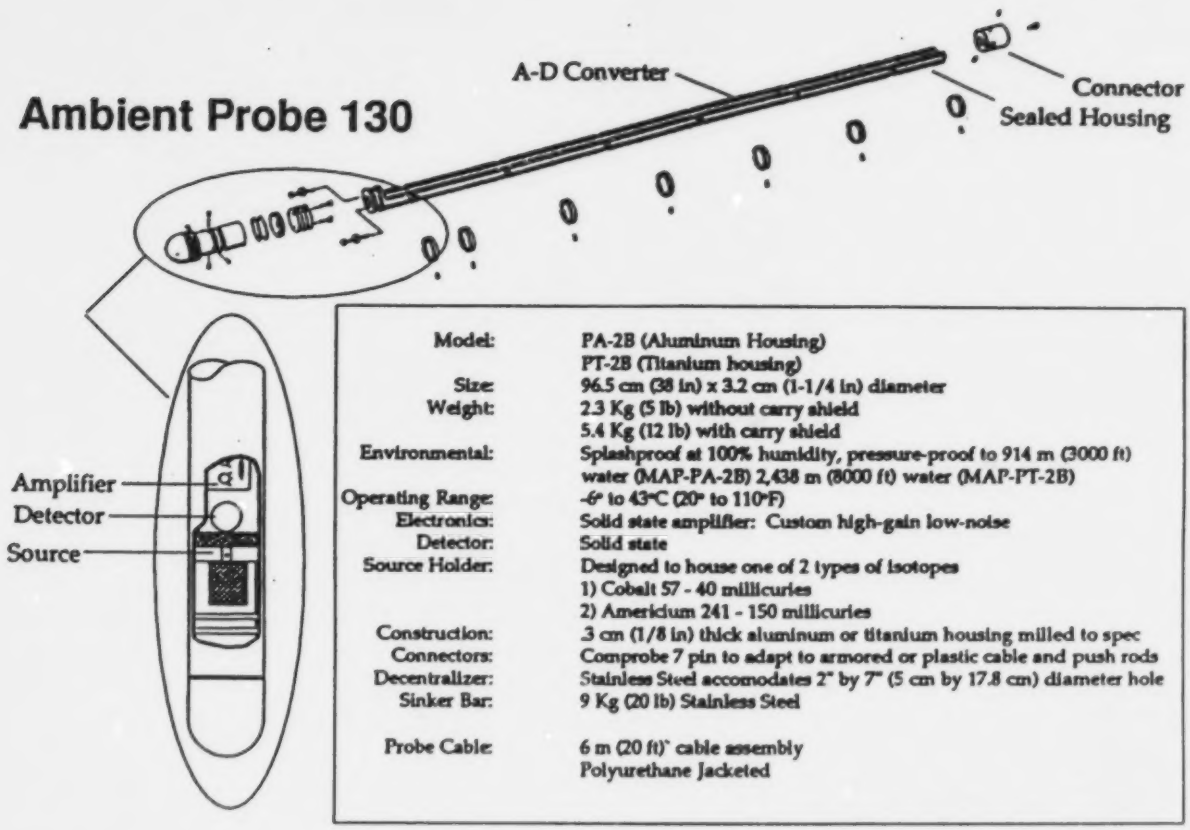
Model:	MAP-FA-2C
Size:	33.7 cm (13 in)
Weight:	1.6 Kg (3.5 lb)
Environmental:	Splashproof at 100% humidity
Temperature:	-6° to +43° (20° to 110°F) operating range
Electronics:	Solid state amplifier: Custom High Gain, Low Noise
Detector:	Solid state
Source Holder:	Designed to house one of 2 types of radioactive isotopes 1) Cobalt 57 - 40 millicuries 2) Americium 241 - 150 millicuries
Safety:	Removable on-off key for source holder
Connector:	13 pin Glenair, pressure proof
Grip:	Rubber cushioned pistol type
Construction:	6061 Aluminum
Face Assayer Cable:	6 m (20 ft) special custom electronics cable Polyurethane Jacketed

Cryo-Scanner 101



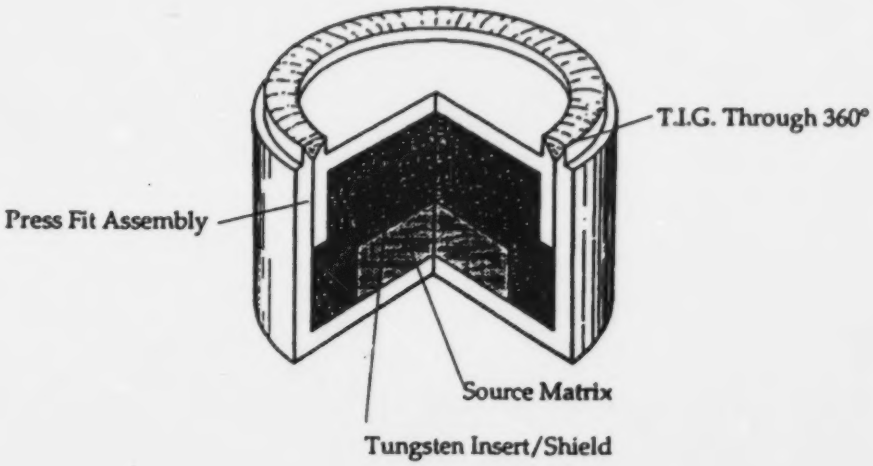
Model:	MAP-CS-1A
Performance Specifications:	Operating Time: Dewar 8 hour, Battery 4 hours
Operating Features:	Rate light, on-off/other light, trigger, , assay on-off/one hand operations, hi voltage location in scanner
Durability:	Hi-impact resistant 3' drop, safety-nonexplosive, water risistant, serviceable and operable
Size:	L = 10-1/4" x W = 4-1/4" x H = 9-1/2"
Weight:	4 pounds empty
Environmental:	Splashproof at 100% humidity
Electronics	preamplifier, high gain/low noise high voltage power supply, integral indicator lights, LED light emitting diodes
Detector:	Cryogenically cooled solid state detector
Source	Cobalt 57 Sealed Source
Construction:	Dewar: Welded Alumunum Carrier: Aluminum Shutter mechanism: Machined tungsten alloy Front: Rubber boot
Safety:	Non-explosive (LN vent in all directions, 100% back-up venting), intrinsically safe, positive off/on, unattended auto-off
Cable:	6 foot cable with connectors on scanner

Ambient Probe 130



Model:	PA-2B (Aluminum Housing) PT-2B (Titanium housing)
Size:	96.5 cm (38 in) x 3.2 cm (1-1/4 in) diameter
Weight:	2.3 Kg (5 lb) without carry shield 5.4 Kg (12 lb) with carry shield
Environmental:	Splashproof at 100% humidity, pressure-proof to 914 m (3000 ft) water (MAP-PA-2B) 2,438 m (8000 ft) water (MAP-PT-2B)
Operating Range:	-6° to 43°C (20° to 110°F)
Electronics:	Solid state amplifier: Custom high-gain low-noise
Detector:	Solid state
Source Holder:	Designed to house one of 2 types of isotopes 1) Cobalt 57 - 40 millicuries 2) Americium 241 - 150 millicuries
Construction:	.3 cm (1/8 in) thick aluminum or titanium housing milled to spec
Connectors:	Comprobe 7 pin to adapt to armored or plastic cable and push rods
Decentralizer:	Stainless Steel accomodates 2" by 7" (5 cm by 17.8 cm) diameter hole
Sinker Bar:	9 Kg (20 lb) Stainless Steel
Probe Cable:	6 m (20 ft)` cable assembly Polyurethane Jacketed

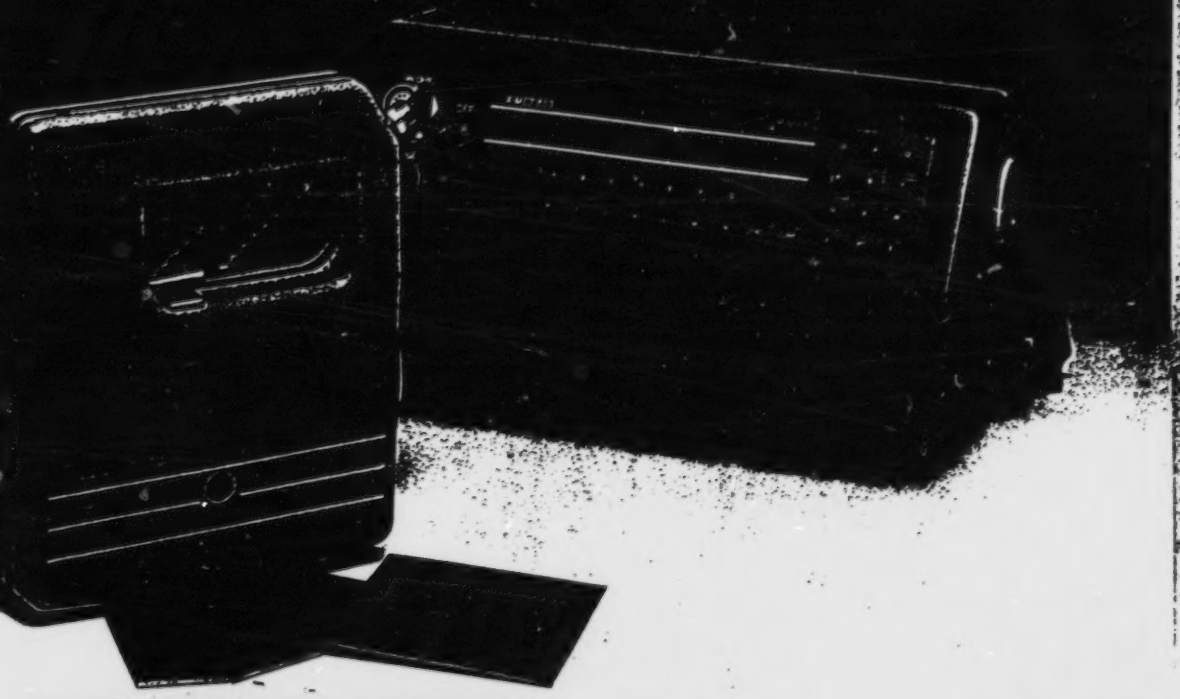
Source Holder



Source Matrix:	Vitreous ceramic fused to the tungsten insert forming a ceramic glaze
Source Type:	Americium 241, Cobalt 57, 40 mci
Source Life:	Americium 247 years, Cobalt 12 - 15 months

LE X-MET D'OUTOKUMPU ELECTRONICS

RAPID METAL SORTING and ANALYSIS by X-RAY FLUORESCENCE



Portable X-MET Alloy Analysis System provides positive material identification

outokumpu ELECTRONICS

X-MET XRF analyzers

INTRODUCTION

Fast and accurate material identification is required in many areas of the metals industry, including production, fabrication, inventory control and scrap sorting. X-ray fluorescence spectrometry has, over the last twenty years, gained the recognition of metallurgists as a significant tool in material identification. The speed, reliability, and non-destructiveness of x-ray fluorescence spectrometry make it suitable not only for laboratory applications, but also for field and plant use.

The successful expansion of x-ray fluorescence analysis from laboratory to plant environments was prompted by the development of portable analyzers made possible by:

(i.) the use of small, sealed radioisotope sources used to excite the characteristic x-rays of the sample;

(ii.) the availability of powerful microprocessors; and

(iii.) the use of rechargeable batteries to make the instrument independent of AC power.

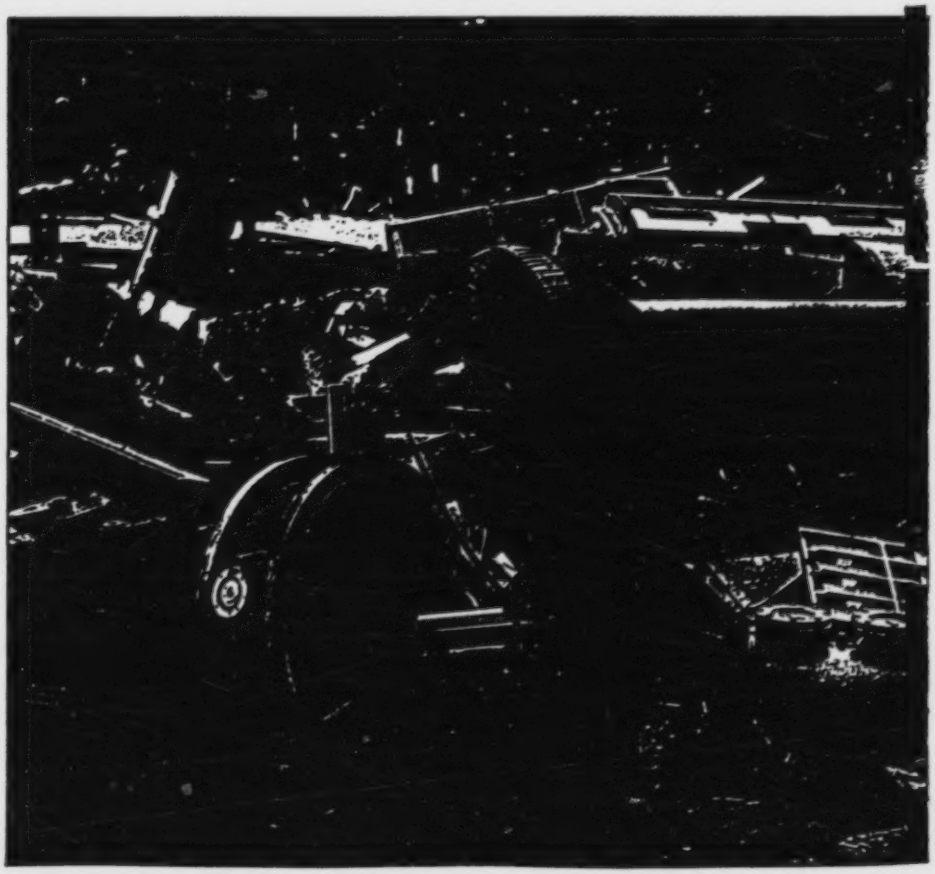
Outokumpu's X-MET x-ray fluorescence analyzer makes use of these developments as well as the most recent advances in microprocessor technology. The X-MET makes it possible to perform complex and simultaneous analysis of the x-ray spectra from the sample using only a battery powered x-ray analyzer. The X-MET also allows for data storage and processing, a task previously assigned to an off-line computer.

A careful examination of the specifications of thousands of alloys currently used reveals that there are 40 to 50 elements involved in the alloying process, with 10 to 20 typically present in any given alloy. In comparison, the X-MET is capable of measuring all 80 of the elements in the periodic table from atomic number 13, aluminum, through atomic number 92, uranium.

Unlike other systems which are limited to 21 or fewer elements and fewer types of alloys, the X-MET is extremely versatile. This advanced design truly represents a significant benefit of the new generation portable alloy analysis systems.

The state-of-the-art X-MET portable alloy analysis system is powerful yet simple to use. It can be factory calibrated to provide a direct readout of alloy name in five seconds or less. Many of the 30,000 alloy types in use today are applicable, including:

- ☐ Stainless and High Temperature Steels
- ☐ Chrome Moly Steels
- ☐ Tool Steels
- ☐ Alloy Steels (with greater than 1 % of either Cr, Ni, Cu, Mn, Mo)
- ☐ Nickel Based Alloys (Inconels, Hastelloys, Monels, etc.)
- ☐ Cobalt Based Alloys (Stellites, Haynes, etc.)
- ☐ Copper Based Alloys (Brasses, Bronzes, Cupro-nickels, etc.)
- ☐ Titanium Based Alloys
- ☐ Aluminum Based Alloys
- ☐ Magnesium Based Alloys
- ☐ Zinc and Lead/Zinc Alloys
- ☐ Exotics (Zirconium Alloys, Molybdenum Alloys, etc.)



ALLOY IDENTIFICATION

Alloy identification can be defined as a process of ascertaining those characteristics of a given material by which it is definitively recognizable or known.

Various techniques have been used over the years for alloy sorting or identification. The traditional ones include color recognition, magnetism, spark testing, differences in apparent density, and chemical spot tests. More sophisticated methods are based on thermoelectricity and optical emission spectroscopy. In general, these methods require an experienced operator to complete the identification, based on the results of the measurement. The same applies to a conventional full scale chemical analysis of an alloy, which must be followed by a search through composition tables to find the matching alloy name or grade designation.

The portable, microprocessor-based X-MET offers a real breakthrough by relieving the operator from decision making. All that is necessary for analysis is to expose the sample to the instrument for a few seconds, and then read the final identification from the display or printout. Search-match technology is employed which eliminates the need for analysis and judgement procedures.

The X-MET provides direct storage of up to 400 precalibrated alloy signatures, and easy replacement by the user can be done on the spot as new alloy identification needs arise. Reference signatures may be custom named for maximum user convenience. Labels such as bin number, serial number, melt number, etc. may be used in place of, or in addition to, alloy common name and/or alloy proprietary name.

In addition to a rapid and positive identification, the X-MET is capable of providing alloy elemental composition [i.e., concentration of major alloying elements displayed as percentages with their respective element symbol(s)] in about 20 seconds, depending on precision and accuracy needed.

With mislabeling of delivered alloy materials occurring from a few percent up to 10 % or more, and with the chance of mixups on production floors, in salvage operations, on jobsites, etc., the economic and product liability concerns increasingly justify investment in such rapid, positive identification devices.

PORTABLE X-RAY FLUORESCENCE ANALYSIS

X-ray fluorescence spectrometry is a comparative analytical technique which utilizes the physical principles of the interaction of x-rays or gamma rays with matter. When a sample is exposed to a beam of low energy (1 to about 100 keV) x-rays or gamma rays, the main result is excitation in the sample of the characteristic x-rays of its elements. It is therefore possible to analyze the sample both *qualitatively* (recognition of elements by their unique x-ray patterns) and *quantitatively* (amount of element in the sample is proportional to the intensity of its characteristic x-rays).

The X-MET portable x-ray analyzer, configured for alloy analysis and identification, consists of a hand-held probe and an electronic unit. The probe contains an x-ray source to excite the sample, and a detector which resolves the x-rays and measures their intensities. The electronic unit accepts the signal from the probe, performs all necessary data processing and displays the result. It also contains the power supplies, operator interface and an I/O port for peripherals such as a printer, data logger or personal computer (PC).

The preferred source for a hand-portable instrument is a sealed radioisotope which emits x-rays or low energy gamma rays. Such sources are rugged, free from drift problems and very compact. Typical sources are only 8 mm in diameter by 5 mm thick, weighing about 2 grams. Their output is about 6 orders of magnitude less than that of an x-ray tube, which results in only minimal potential radiation hazard (for the same reason, the use of classic wavelength-dispersive crystal spectrometers with high x-ray tube intensities and high power requirements is impractical).

For optimum performance, x-rays must be measured with high geometrical efficiency, and the detector must be capable of discriminating between x-rays from neighboring elements without further significant loss of x-ray photons. Gas-filled proportional counters have proven themselves over the years as the most reliable detectors used in portable x-ray analyzers.

Until recently, the resolution of proportional counters has not been good enough to avoid the need for balanced filters. However, new developments in proportional counter technology (as used in the X-MET) have yielded detectors which significantly improve the resolution (12-14 % for the MnK line). This, coupled with a superior microprocessor (Motorola 68000) for spectral processing, has resulted in the availability of the hand-portable X-MET x-ray fluorescence analyzer capable of simultaneous multielement analysis.

X-MET 880

THE X-MET SYSTEM

With the X-MET portable alloy analysis system, measurements are totally non-destructive and can be made under extremes of environmental conditions ranging from high dust indoor environments to very cold, hot or wet outdoor environments.

The unit features a slim-line lightweight weatherproofed probe and hermetically sealed electronic unit totalling only 8.5 kg. It is designed to fit in a small water repellant backpack for user convenience in field transport. Power for field operations is received from long lasting lead gel-cell, plug-in rechargeable batteries that easily last over 10 hours of continuous use, without the disadvantage of "memory" effect such as is typical of Ni-Cad type battery systems.

The X-MET system has proven its worth in hundreds of installations throughout the world. It has prevented thousands of costly mix-ups and potential liability problems by providing decision-making data for metallurgical specification analysis.

KEY FEATURES

The keys to such a wide range of capabilities and such high performance in a portable system are:

1.) The high resolution proportional detector which gives good performance and high reliability at ambient temperatures without the need for x-ray filters or liquid nitrogen dewars.

2.) The microprocessor/software/electronics package which takes full advantage of the fundamental improvements in detection capability, while allowing simple straightforward man/machine interfacing and providing powerful search/match pattern recognition techniques for alloy identification. In addition, the microprocessor provides the capability for on-line computation of elemental alloy composition.

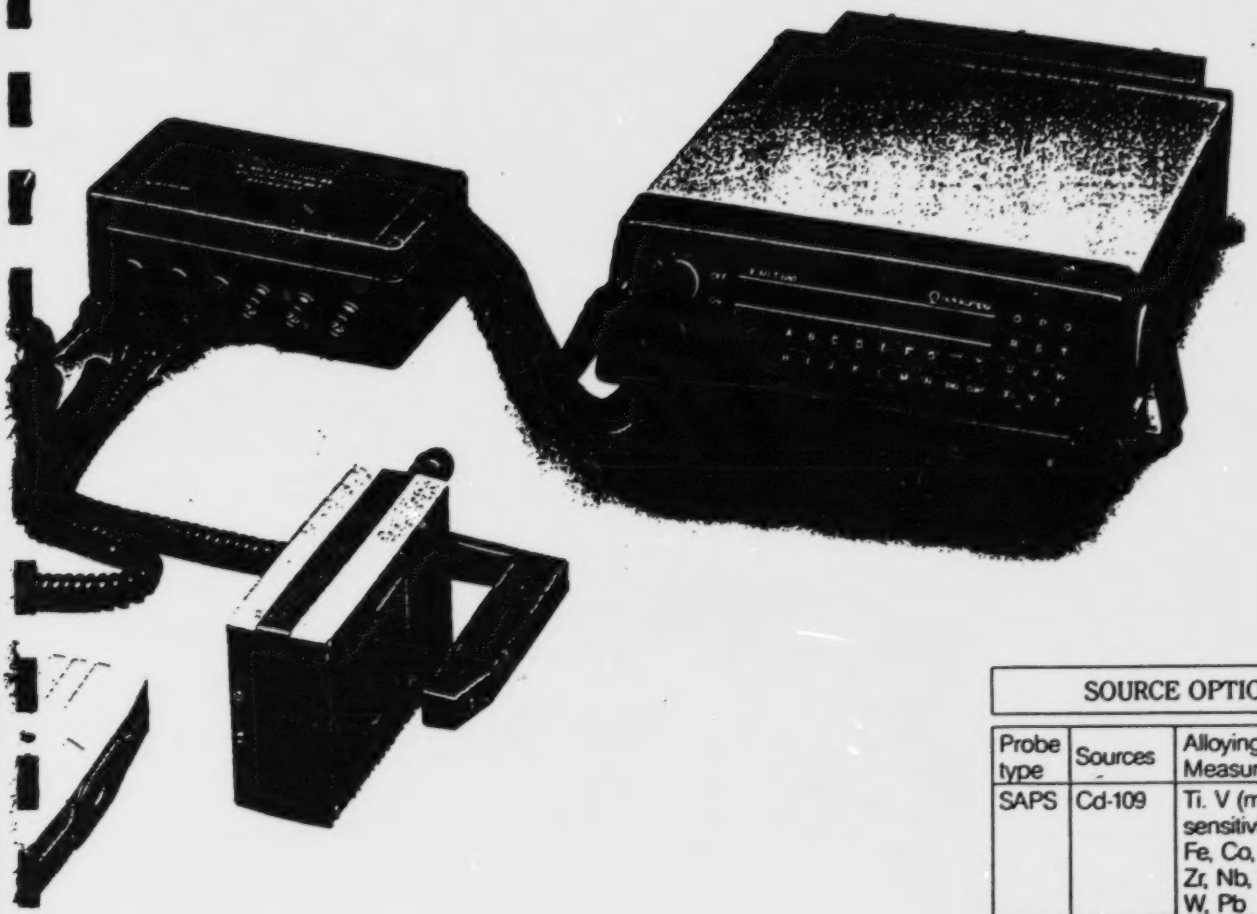
FIELD PROGRAMMING

With a fully calibrated unit (as supplied from the factory) operator training is minimal, and routine use is extremely simple. However, unlike other portable alloy analyzers of earlier design, the X-MET allows for easy and rapid field reprogramming. A special code provides operator access to programming functions which allow on-the-job customized calibrations for either the identification mode (alloy type) or the assay mode (composition readout). Addition of references in the I.D. mode is extremely simple. (Type in "ADD", then measure a reference standard for 100 to 200 seconds). Calibration training, to allow the user to create special or custom calibrations in the assay mode, is provided by the X-MET representatives worldwide.

OPTIONAL ITEMS

To facilitate field programming, Outokumpu offers a set of 100 reference alloys, all of which include certificates of analysis showing the participating labs and verifying each laboratory's method based on NIST (National Institute of Standards and Technology) traceability. The set covers the 100 most commonly used alloys, that also represent the optimum calibration suite for each alloy type. (Request Brochure No. BNRM-1 for further alloy standards information.)

To document the data from X-MET, Outokumpu offers a lightweight, portable, battery operated terminal/printer, which plugs directly into the X-MET. For further data handling needs, the X-MET results may be collected on a plug-in data logger, for later readout, or may be interfaced directly to a PC system. Outokumpu can supply standard software to facilitate use and enhance PC data capture, as well as, data reduction.



EXCITATION SOURCE OPTIONS

The system is routinely configured with a Cd-109 excitation source which provides excellent performance for common alloying elements such as chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), niobium (Nb), molybdenum (Mo), zirconium (Zr), tungsten (W) and lead (Pb). A dual-source probe is also available which can contain two excitation sources, such as Cd-109 and Fe-55. With this combination, the performance of the Cd-109 excitation source, for the elements listed above, is maintained; while the elements titanium (Ti) and vanadium (V), which are more efficiently measured using the Fe-55 excitation source, are brought into the "excellent performance" category.

Another example of the benefit of a dual-source probe is the extended element analysis range offered by the combination of Am-241 and Cd-109. This source combination extends the elemental analysis range so that it includes tin (Sn) in, for example, copper and titanium based alloys. The combination of Am-241 and Cm-244 sources allows analysis for elements in the same spread as the Am-241/ Cd-109 range, but with slightly reduced sensitivity for Nb and Mo and somewhat increased sensitivity for Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, W and Pb. In addition to the important capability of Sn analysis, combining the Am-241 source with either Cd-109 or Cm-244 allows analysis for other so-called "heavier"** elements, which may be important for some alloys.

SOURCE OPTIONS

Probe type	Sources	Alloying Elements Measured
SAPS	Cd-109	Ti. V (moderate sensitivity), Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Hf, Ta, W, Pb
DOPS	Cd-109, Fe-55	Same as a single Cd-109 source, plus excellent performance for Ti, V
DOPS	Cd,109, Am-241	Same as a single Cd-109 source, plus Rh, Pd, Ag, In, Cd, Sn, Sb
DOPS	Cm-244, Am-241	Same as Cd-109/Am-241 dual source w/slightly reduced sensitivity for Nb and Mo, increased sensitivity for Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Hf, Ta, W, Pb
SLPS	Fe-55	Al, Si, P, S, Ti*, V*, Cr*

SAPS = SURFACE ANALYSIS PROBE
DOPS = DOUBLE SOURCE PROBE
SLPS = SURFACE LIGHT ELEMENT PROBE
*SLPS with Fe-55 provides the highest possible sensitivity (see table 6).

** K shell x-ray energies above 18 keV are considered to arise from "heavy" elements. For example, atomic numbers 44 thru 56 (Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs and Ba).

APPLICATIONS

Examples of Applications are:

- ☐ Incoming Inspection
- ☐ On-Site Alloy Verification
- ☐ Quality Control
- ☐ Stock Control
- ☐ Scrap Upgrade and Classification
- ☐ Melt Analysis
- ☐ Weld Analysis
- ☐ Maintenance Assessment
- ☐ Construction Site PMI (Positive Material Identification)

Products analyzed include all sizes, shapes, and finishes.

Examples of Products Analyzed are:

- ☐ Sheets
- ☐ Ingots
- ☐ Billets
- ☐ Castings
- ☐ Plates
- ☐ Rods
- ☐ Tubes
- ☐ Bars
- ☐ Bolts
- ☐ Blades
- ☐ Fasteners
- ☐ Valves
- ☐ Tanks
- ☐ Sludges
- ☐ Turnings
- ☐ Powders
- ☐ Liquid Digestions
- ☐ Cutting Oils

For most products, little or no sample preparation is required: simply place the probe on the material, pull the trigger for a few seconds, then read out the results.

Examples of Applicable Industries include:

- ☐ Fossil and Nuclear Power
- ☐ Metallurgical Manufacturing Industry
- ☐ Metal Service and Distribution Centers
- ☐ Metal Scrap Recycling Operations
- ☐ Foundries
- ☐ Analysis Service Labs
- ☐ Chemical Process Industries
- ☐ Construction Engineering
- ☐ Refining and Petrochemical
- ☐ Pulp and Paper
- ☐ Metals Fabrication
- ☐ Military Hardware

UNIQUE CAPABILITIES

The standard alloy system consists of a 1.5 kg trigger-actuated probe with 6×21 mm measurement area (other sizes optional), an excitation source (or sources with dual source probe) and a 7 kg microprocessor-based electronic unit which processes and stores all data. The probe can measure sizes both smaller and larger than the measuring aperture while maintaining correct identification (I.D.) results.

Although the probe must be in contact with the sample and must cover the measuring aperture for quantitative results (elemental composition), the alloy sort (I.D.) mode results are automatically corrected for undersize samples (below 6×21 mm) and non-contacted samples (up to 19 mm away from the probe). One extreme example of an undersize sample that identifies correctly in 5 seconds with no special procedure (such as taping a bundle of rods together) is the separation of 0.8 mm diameter Inconel welding rods.

The standard alloy system can be upgraded any time by the addition of a Surface Light Element Probe. The unique capability to analyze "light"*** elements with a portable analyzer with no "special" consideration (such as helium purge or vacuum path) allows such previously unattainable field analyses as sulphur (S) in steel, silicon (Si) in aluminum, Si and Ti in nickel based alloys, etc.

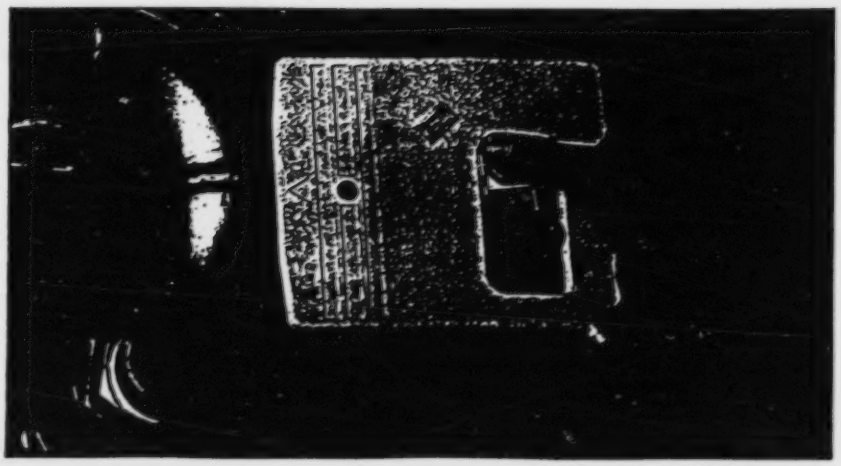
It is well known that the stainless steels 303 and 304 differ only by 0.3 % sulphur, which makes separation of these two grades extremely difficult and challenging. However, the identification mode handles this task very well with the use of a surface light element probe and a Fe-55 source. With this configuration, the X-MET can positively identify 303 from 304 with 100 % success. A similar example is the pair 410 and 416 stainless steel, which also differs by 0.3 % sulphur and can be handled in the very same manner. It should be noted that sulphur and the other elements of atomic number greater than 12 can be measured with this probe using an air path.

In one case, this light element probe proved its excellent sensitivity for titanium in steels by analyzing the residual metal particles in sandpaper and consistently identifying 304-vs-321 correctly in 5 seconds based on the Ti signal from the alloy particles retained on the sandpaper (request the detailed report from your sales agent). With such high sensitivity for titanium, the task of separating 304 from 321 can be accomplished in just one (1) second with 100 % confidence.

Using a standard surface analysis probe with Cd-109 source, the sorting routine has proved itself also to work with a 100 % success rate on separation of stainless steel 303 and 303Se, where the only difference is 0.3 % selenium.

PERFORMANCE

Examples of performance for a wide range of applications are given in the following tables. Note that the data given represent typical precision and RMS values. In many cases, even better values can be achieved.



*** K shell x-ray energies below 5 keV are considered to be those of the light elements, for example, atomic numbers 13-23 (Al, Si, P, S, Cl, Ar, K, Ca, Sc, Ti and V).

TABLE 1. SUMMARY OF THE RESULTS OF IDENTIFICATION PROCEDURE

Alloy Group in Model	Measured Elements	Identification Results for Typical Useage % Feasible
Nickel Alloys (26 ref.)	Ti, Cr, Fe, Co, Ni, Cu, Nb, Mo, W	100
Copper Alloys (5 ref.)	Mn, Fe, Ni, Cu, Zn, Pb, Sn	90 to 100
Stainless and High Temp. Steels (26 ref.)	Ti, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo	90 to 100
Cr/Mo Steels (6 ref.)	Cr, Fe, Ni, Mo	95 to 100
Carbon and Low Alloy Steels (9 ref.)	Cr, Fe, Ni, Mo	65
Titanium Alloys (16 ref.)	Ti, V, Cr, Mn, Cu, Zr, Mo	95 to 100
Aluminum Alloys (8 ref.)	Ti, Cr, Mn, Fe, Cu, Zn	90 to 100

Within-the-group identification

Several individual models were set up for various alloy groups using a probe equipped with a 5 mCi Cd-109 source. In each model first a library of reference alloys was created by measuring each reference for 200 sec. Then each reference sample was measured, as an unknown, at least ten times for 5 sec. and the percentage of correct or incorrect identifications was recorded. The percent correct or incorrect identification within each alloy group was calculated for all alloys tested within a given alloy group. The results are listed in the above Table.

TABLE 2. X-MET SYSTEM PERFORMANCE DATA FOR CARBON, LOW ALLOY AND Cr/Mo STEELS

MEASUREMENT CONDITIONS: Probe: DOPS; Slot Aperture, Dual Source Meas. Time: 300 sec.						
Source	Cm-244					Cd-109
Element	Cr	Mn	Fe	Ni	Cu	Mo
Concentration Range	0—9 %	0—1 %	90—100 %	0—3.5 %	0—1 %	0—1 %
RMS Error a)	.07 %	.13 %	.45 %	.2 %	.06 %	.015 %
Precision of b) Measurement	.06 %	.13 %	.24 %	.1 %	.015 %	.010 %

a) Root Mean Square Error ± around the calibration line fitted (LSQ Method) to the experimental data points.
b) One standard deviation due to counting statistics; value reported is valid for the measurement time given in top of the table.

TABLE 3. X-MET SYSTEM PERFORMANCE DATA FOR HIGH TEMPERATURE AND STAINLESS STEELS

MEASUREMENT CONDITIONS: Probe: DOPS; Slot Aperture, Dual Source Meas. Time: 100 sec.							
Source	Fe-55	Cd-109					
Element	Ti	Cr	Mn	Ni	Cu	Nb	Mo
Concentration Range	0–2 %	0–25 %	0–15 %	0–35 %	0–35 %	0–1 %	0–35 %
RMS Error a)	.09 %	.30 %	.40 %	.35 %	.14 %	.01 %	.02 %
Precision of b) Measurement	.05 %	.15 %	.20 %	.35 %	.14 %	.01 %	.01 %

a) Root Mean Square Error ± around the calibration line fitted (LSQ Method) to the experimental data points.
b) One standard deviation due to counting statistics; value reported is valid for the measurement time given in top of the table.

TABLE 4. X-MET SYSTEM PERFORMANCE DATA FOR NICKEL, COBALT ALLOYS

MEASUREMENT CONDITIONS: Probe: SAPS; Slot Aperture Source: Cd-109 Meas. Time: 100 sec.								
Element	Cr	Fe	Co	Ni	Cu	W	Nb	Mo
Concentration Range	0–30 %	0–67 %	0–60 %	0–100 %	0–32 %	0–15 %	0–5 %	0–28 %
RMS Error a)	.65 %	.315 %	.80 %	1.0 %	.40 %	.38 %	.04 %	.18 %
Precision of b) Measurement	.15 %	.20 %	.40 %	.5 %	.30 %	.11 %	.02 %	.18 %

a) Root Mean Square Error ± around the calibration line fitted (LSQ Method) to the experimental data points.
b) One standard deviation due to counting statistics; value reported is valid for the measurement time given in top of the table.

TABLE 5. X-MET SYSTEM PERFORMANCE DATA FOR COPPER ALLOYS (BRONZES & BRASSES)

MEASUREMENT CONDITIONS: Probe: DOPS; Slot Aperture, Dual Source Meas. Time: 100 sec.							
Source	Cm-244					Am-241	
Element	Fe	Ni	Cu	Zn	Pb	Cd	Sn
Concentration Range	0–5 %	0–30 %	60–100 %	0–40 %	0–8 %	0–0.1 %	0–1 %
RMS Error a)	.15 %	.35 %	.45 %	.31 %	.3 %	.020 %	.005 %
Precision of b) Measurement	.1 %	.25 %	.45 %	.25 %	.1 %	.008 %	.005 %

a) Root Mean Square Error ± around the calibration line fitted (LSQ Method) to the experimental data points.
b) One standard deviation due to counting statistics; value reported is valid for the measurement time given in top of the table.

TABLE 6. X-MET SYSTEM PERFORMANCE DATA FOR ALUMINUM ALLOYS

Probe Source	SLPS (Ne)/Fe-55			DOPS (Xe Ar) dual source/CM-244[1] + Am-241[2]						
Time	240 seconds			60 seconds						
Elements	Si	Ti	Cr	Mn[1]	Fe[1,2]	Ni[1]	Cu[1]	Zn[1,3]	Pb[1,3]	Sn[2]
Concentration Range	0–12 %	0–16 %	0–25 %	0–8 %	0–12 %	0–5 %	0–5 %	0–3.5 %	0–3.5 %	0–25 %
RMS Error a)	.22 %	.0015 %	.02 %	.04 %	.04 %	.003 %	.08 %	.06 %	.06 %	.02 %
Precision of b) Measurement	.20 %	.001 %	.005 %	.03 %	.01 %	.004 %	.005 %	.005 %	.005 %	.003 %

a) Root Mean Square Error ± around the calibration line fitted (LSO Method) to the experimental data points.
b) One standard deviation due to counting statistics; value reported is valid for the measurement time given in top of the table.

TABLE 7. X-MET SYSTEM PERFORMANCE DATA FOR CARBON, LOW ALLOY AND Cr/Mo STEELS

MEASUREMENT CONDITIONS:
Probe: SAPS; Slot Aperture
Source: Cd-109
Meas. Time: 300 sec.

Element	Cr	Mn	Fe	Ni	Mo
Concentration Range	0—9 %	0—1 %	90—100 %	0—3.5 %	0—1 %
RMS Error a)	.2 %	.35 %	.45 %	.15 %	.015 %
Precision of b) Measurement	.2 %	.2 %	.3 %	.1 %	.010 %

a) Root Mean Square Error ± around the calibration line fitted (LSO Method) to the experimental data points.
b) One standard deviation due to counting statistics; value reported is valid for the measurement time given in top of the table.

TABLE 8. X-MET SYSTEM PERFORMANCE DATA FOR TITANIUM ALLOYS

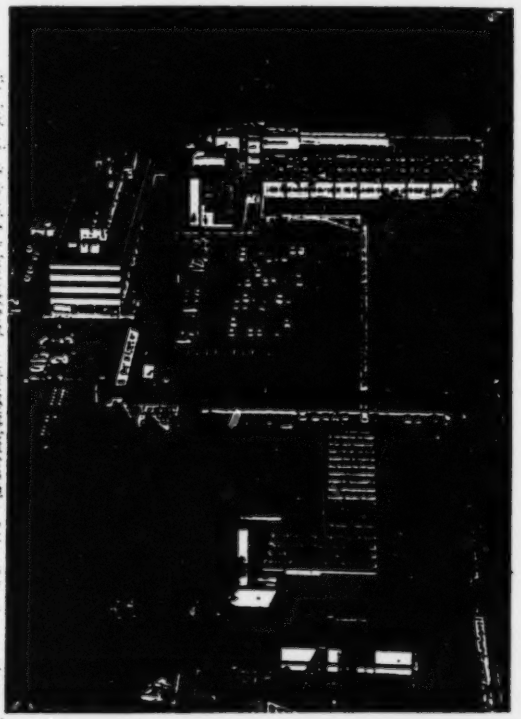
MEASUREMENT CONDITIONS:
Probe: SAPS
Source: Cd-109
Meas. Time: 100 sec.

Element	V	Cr	Ni	Zr	Nb	Mo
Concentration Range	0—8 %	0—6 %	0—1 %	0—5 %	0—2 %	0—15 %
Precision of Measurement a)	.2 %	.2 %	.3 %	.02 %	.001 %	.03 %

a) One standard deviation due to counting statistics; value reported is valid for the measurement time given in top of the table.

Outokumpu Electronics, a Division of Outokumpu Oy

Outokumpu Electronics is a division of Outokumpu, an international multimetal group. Outokumpu has an annual turnover of approx. USD 2 billion, 15,000 employees and operations in over 20 countries.



The Electronics Division comprises two units operating in Finland, Instruments and Systems, as well as the American subsidiary Princeton Gamma-Tech, Inc.

Outokumpu Electronics' Product Range

INSTRUMENTS

- X-MET portable and benchtop analyzers
- METOR metal detectors
- IMIX imaging and X-ray microanalysis systems
- Gamma-ray and X-ray detectors

SYSTEMS

- COURIER on-line X-ray analyzers
- BELTCON on-line belt analyzer
- OTI automatic titrator
- AOP/PROSCON process control and management systems

Printed in Finland by H.-Paino Oy 1990

ANNEXE - B

INFORMATION TECHNIQUE SUR LES APPAREILS À FLUORESCENCE-X (SPECTROMÉTRIE À ÉNERGIE DISPERSIVE)

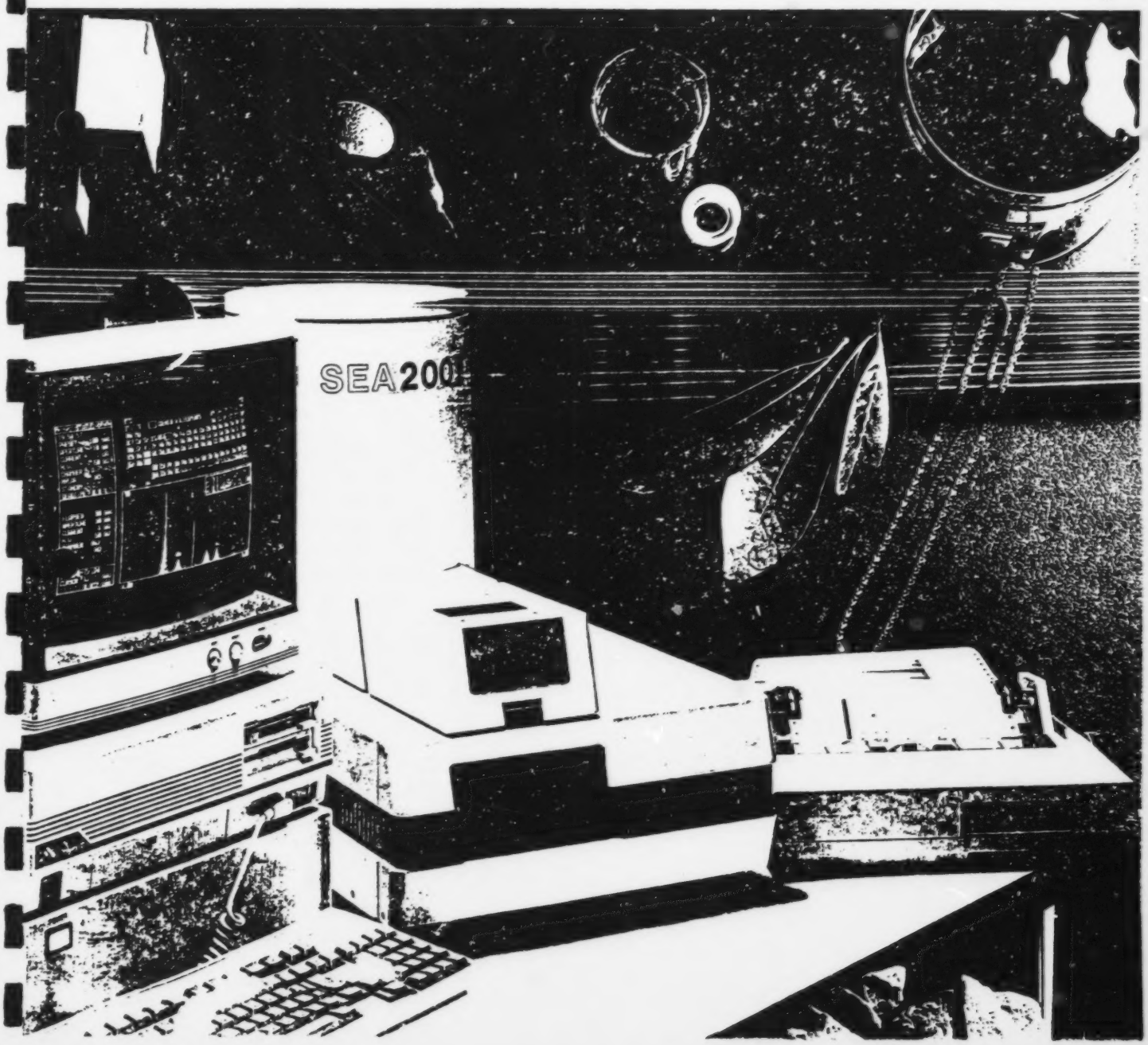
SEIKO I ELEMENT MONITOR
DE SEIKO INSTRUMENTS INC.

SEIKO I

Seiko Instruments Inc.

ELEMENT MONITOR

Bench Top X-ray Fluorescence Analyzer SEA2001



Product Support Specialist
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Fax (416) 632-9327

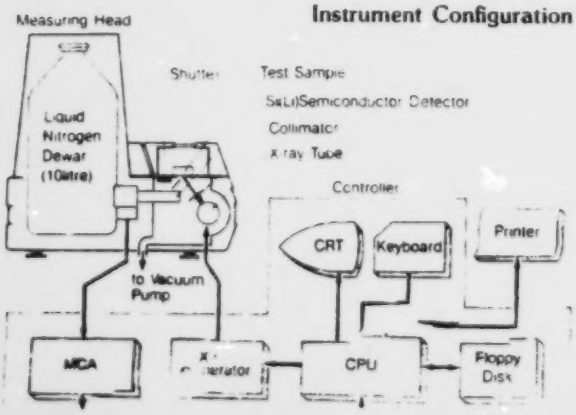
Economical, ...Innov

Energy Dispersive X-ray Analyzer

The energy dispersive X-ray analyzer (EDS) is our natural choice for making a handy, quick, non-contact, non-destructive, and high precision instrument for elemental analysts. As it requires only small X-ray intensities, the EDS is very simple in structure and very safe X-ray leakage. Also, unlike the wavelength dispersive X-ray analyzer, it does not need a crystal or goniometer.

Seiko Instruments has developed an original Si(Li) Semiconductor Detector. This new detector has made the SEA-2001 much smaller than conventional EDS machines. Operation is also very simple. The user will never know, nor need to know, how much X-ray technology is packed inside this compact, easy-to-operate, but high-precision Element Monitor.

Instrument Configuration

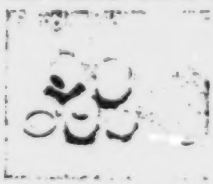


Wide Application Range

The SEA-2001 Element Monitor can detect all elements from Na to U simultaneously and calculate their composition within a very short time. The measurement is non-destructive, so the Element Monitor can be used for testing precious metal products too. No special preparation of the sample is necessary.

Simply place your sample into the measuring chamber. Select the best analysis conditions, and press the start button. These 3 procedures are all that is necessary to obtain highly reliable data.

Any type of sample can be measured with the SEA-2001. Seiko Instrument's special sample holder is available for liquid and powder samples. This ease of sample preparation is another big reason why the SEA-2001 Element Monitor is becoming a standard tool for quick elemental analysis.

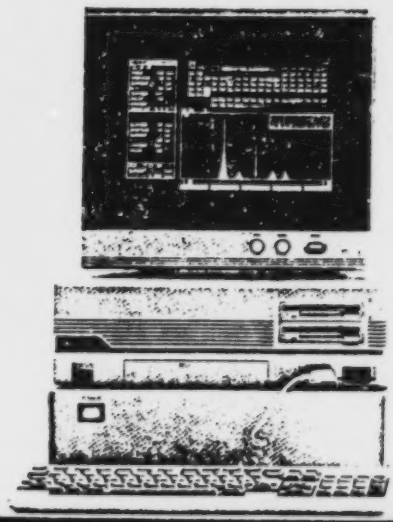


The SEA-2001 Element Monitor-the standard tool for all types of elemental analysis!

The Element Monitor is already being used by the following customers.

- **Jewelry makers:** Au, Ag, Pt, etc., precious metal identification composition measurement.
- **Electronics component makers:** Instant cheking of plating solution main element composition. Raw material analysis.
- **Pharmaceutical product manufactures:** Elemental analysis of botanical samples.

Quick and Easy Elemental
vation from Seiko Instrum

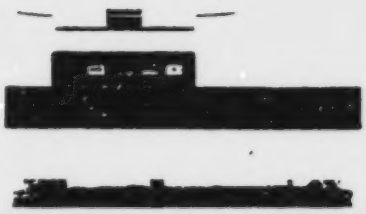


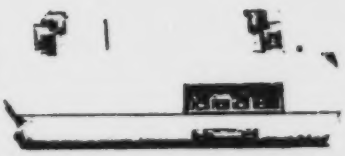
2001

SEA-2001
Software

Learn Mode

Analysis Mode
Edit Mode
Saving Mode
Print-out Mode
MS/DOS Mod





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Mode

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OS Mode

Qualitative Analysis
Quantitative Analysis

Automatic
Manual
F.P.T.
Calibration Method

One-Standard
Non-Standard

Fundamental Parameter Method Makes High Precision Analysis Much Easier

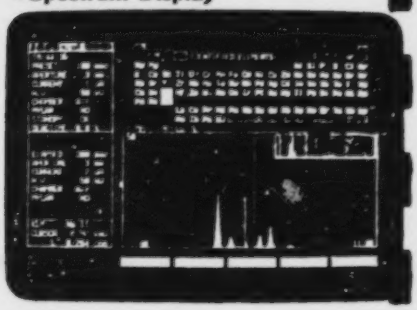
The fundamental parameter method is an entirely different method of qualitative analysis from the calibration method. The basic parameters of each element are stored in the Element Monitor's memory. X-ray fluorescence information obtained by measurement based on these parameters is used to calculate precise quantitative values for each element. F.P.T. makes measurement possible even when there are no standard samples. Of course, if a standard sample is available, much higher accuracy measurements can be made.

Example: Analysis of alloys (Brass)

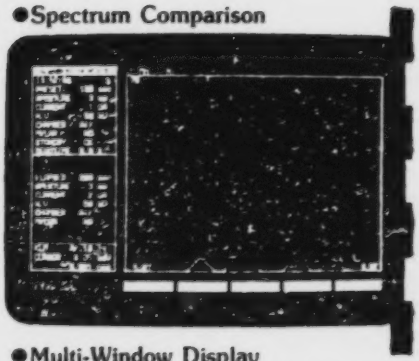
Elements	Method	A	B	C	D
Cu	Chemical Analysis	60.96%	56.28%	60.37%	58.30%
	Non-Standard	60.81	56.14	60.38	58.30
	One-Standard	60.86	—	60.35	58.37
Zn	Chemical Analysis	35.35	40.35	36.83	38.78
	Non-Standard	35.25	40.05	36.81	38.26
	One-Standard	35.51	—	37.04	38.56
Pb	Chemical Analysis	3.30	3.00	2.46	2.85
	Non-Standard	3.47	3.41	2.45	3.28
	One-Standard	3.05	—	2.15	2.89
Sn	Chemical Analysis	0.25	0.23	0.22	0.04
	Non-Standard	0.19	0.14	0.13	0.05
	One-Standard	0.31	—	0.20	0.08
Fe	Chemical Analysis	0.14	0.14	0.12	0.03
	Non-Standard	0.17	0.15	0.15	0.06
	One-Standard	0.31	0.14	0.14	0.05
Ni	Chemical Analysis	—	—	—	—

Big, Colorful, and Easy-to-Understand Display

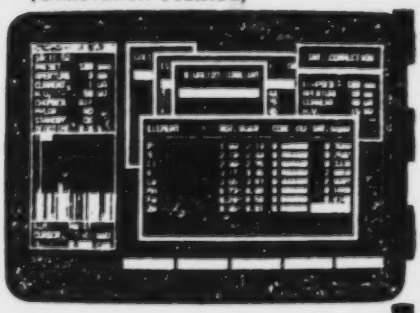
●Spectrum Display



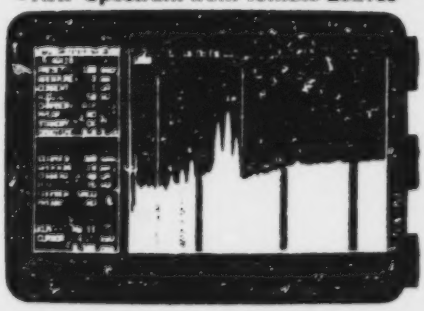
●Spectrum Comparison



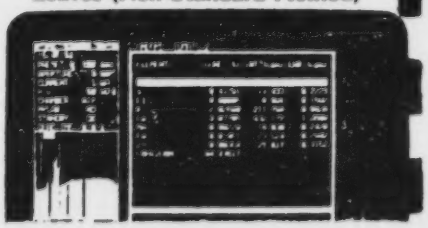
●Multi-Window Display (Calibration Method)



●XRF Spectrum from Tomato Leaves



●Quantitative Analysis of Tomato Leaves (Non-Standard Method)



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Science Made Technology. "Seiko I" Made It Handy!

At Seiko Instruments Inc., during our long experience in elemental analysis instrumentation in Japan where we gained extensive knowledge concerning X-ray technology products for users throughout the world, we have kept asking ourselves- "What is really needed by an analyst?"

Reliable Data!

What an analyst, whether a specialist or non-specialist, really needs is reliable data from the analysis instrument. But, do high-performance analytical instruments always have to be so difficult to understand? Do they have to be complicated to operate? Should the user be required to have specialized knowledge and skill for sample preparation?

No! We believe this is not necessary.

Just Like Our Watches

The SEA-2001 Element Monitor is our answer to all of the above questions. Progress in science and high technology has made it possible to analyze elements with high precision. Seiko Instruments has made it easy for anyone with the Element Monitor.

Just as high-precision wristwatches have become standard time-keeping tools for ordinary people, now Seiko Instruments introduces the SEA-2001 Element Monitor; the standard elemental analysis tool for every analyst's workplace!

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Targe
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LN2
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Qual
Quan
Learn
Data
Produ

●Detectable elements (range of analysis)

	Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIII			Ib	IIb	IIIa	IVa	Va	VIa	VIIa	0
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

●Specifications

Sample Chamber

Sample size:	Max 120mmφ×70mm'
Sample form:	•Solid •Liquid •Powder (in sample holder)
Atmosphere:	•Air •Vacuum •Helium (option)
Rotary pump:	10^{-1} Torr

X-ray Generator

Voltage:	15kV & 50kV selectable
Current:	0~255μA (Max. 3W)
Target:	Rh (Mo target is available as an option)
Cooling method:	Air cooling
Aperture size:	•10mmφ •3mmφ •1mmφ (using mask)

Detector

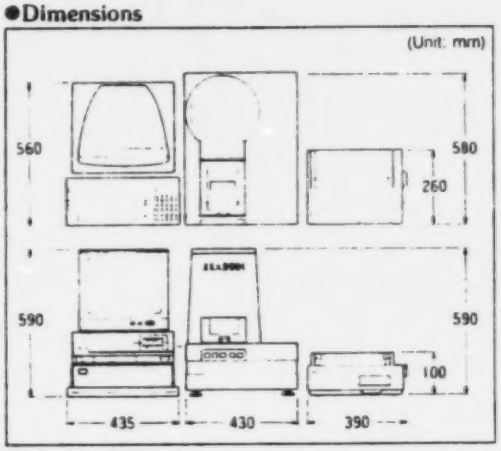
Type:	Si (Li) Semiconductor Detector
Dewar capacity:	10ℓ
LN_2 consumption:	Less than 1.0ℓ/day

Software

Qualitative analysis:	Automatic and Manual
Quantitative analysis:	•Fundamental Parameter Method (Non standard) •Fundamental Parameter Method (One standard) •Calibration method
Learn program:	Automatic operation program
Data output printer:	External printer

Product specifications subject to change without notice.

●Dimensions



●Installation

Power Source:	100V AC ±10% 1.5kVA
Dimension/Weight	
Measuring head:	480 (W) × 660 (D) × 590 (H) mm, 50kg
Controller:	435 (W) × 560 (D) × 590 (H) mm, 13kg
Printer:	390 (W) × 281 (D) × 141 (H) mm, 6kg

CANADIAN REPRESENTATIVE
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(416) 632-9494 L7R 3Y2

Seiko Instruments Inc.
6-31-1, Kameido, Koto-ku, Tokyo, 136 Japan
Telephone: 03-637-1393 Telex: 2[illegible] D SEIKO J

SYRANO 3 (BRGM) DE
INTERMETRIX SYSTEMS INC.

*SYRANO 1
*SYRANO 2
*SYRANO 3

BRGM

ARE **X-RAY FLUORESCENCE** ANALYSIS INSTRUMENTS

WITH THE SYRANO FAMILY
BRGM PROVIDES SERVICES FROM THE OUTSET.
THESE **SERVICES** ARE BASED ON THE SUPPLY
OF INNOVATIVE SIMPLE POWERFUL
AND **PERSONALIZED** INSTRUMENTS

X-RAY FLUORESCENCE

The **SYRANO** family uses X-ray fluorescence energy dispersive spectrometry. Fluorescence is induced in a sample by a low activity radioactive source, detection is by a Si or Si(Li) semiconductor. Mathematical processing of the signal is realized in real time by a Z80 microprocessor integrated in the system.
The contents are displayed on a screen and can be printed.

SERVICES

The ease of operation of **SYRANO** means that the apparatus can be put into the hands of staff without any particular qualification.
Your analysts will thus be relieved of numerous routine tasks while being assured of benefit from constant analytic quality.

PERSONALIZED

The user sets the analytical problems in a schedule of instructions with the possible assistance of **BRGM**.
The instrument, tested beforehand on samples, is only proposed for sale after fully satisfying the conditions required.
The quality of the processing software, its adaptability to the users specific problems, gives **SYRANO** exceptional performance. The personalized calibration is realized by **BRGM** on each instrument.

AN ANALYZING APPARATUS SERVICE

SYRANO IS DESIGNED FOR THE QUANTITATIVE ANALYSIS OF ELEMENTS WITH ATOMIC NUMBER $\geqslant 20$

BRGM also examines any problem concerning the modification and adaptation of the basic apparatus.

*SYstem for Research and ANalysis of Ores.

Instruments developed in collaboration between B[illegible] and **ENERTEC** (subsidiary of **SCHLUMBERGER**) with assistance from **CEE** and **ANVAR**

SYRANO I

PORTABLE APPARATUS

TECHNICAL SPECIFICATIONS

asic instrument comprising a case nalyzer and battery pack) and type Ia obe.

NALYZER CASE

Case dimensions : 30X20X31 cm.
Weight of case : 10.25 kg.
Operating temperature : 0-45 °C.
Electronics : microprocessor and low power circuit C-MOS.
Display : liquid-crystal alphanumeric.
Keyboard : 12 keys with 4 reserved for program selection.
Power supply : rechargeable Ni-Cd batteries (10 hrs working life).
Analytic program capacity : 4 programs (or 8 in option).
AC generator (110/220 Volts; 50-60 Hz).

ROBE (Type Ia)

Weight : 2.250 kg.
Safety ensured by shutter and key
Detector : Ion - impl[illegible] ilicon X-ray detector. Stabilizatic[illegible] eltier effect between 0 and 50°.

SEALED RADIOACTIVE SOURCE

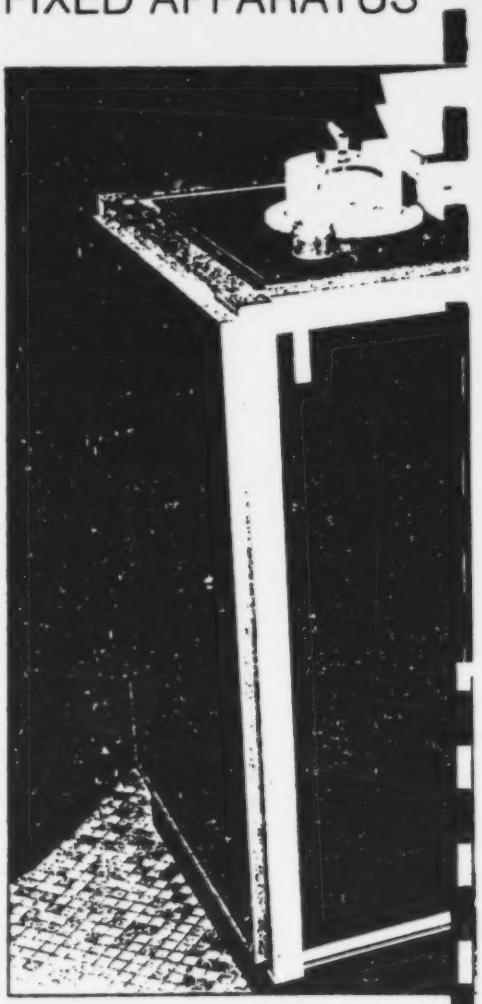
- Fe 55 ; 20 mCi - half life 2.7 yrs.
- Cd 109 ; 10 mCi - half life 453 days.
- Am 241 ; 10 mCi - half life 433 yrs.

OPTIONS

- Printer - travelling crate.
- Second battery pack.
- Generator for recharging 2nd battery pack at remote sites.
- Second probe with another 10 mCi source (Type Ia only).
- Analytical programs beyond the fourth (up to 8 programs).
- Expendable items (on request). Specimen holders (lots of 10) for powders or liquids. Mylar sheets : 36 µm for powders, 10 µm for solutions.

SYRAN

FIXED APPARATUS

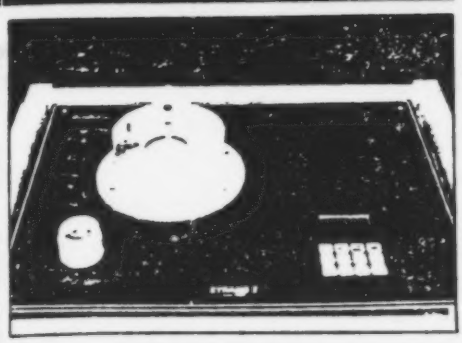


TECHNICAL SPECIFICATIONS

INSTRUMENT AND LIQUID NITROGEN RESERVOIR

- Dimensions : 106X60X81 cm.
- Weight : 120 kg.
- Operating temperature : 0-45 C.
- Display : liquid crystal alphanumeric.
- Keyboard : 12 keys with 4 reserved for analytical program selection.
- Power supply : 110/220 Volts, 50-60 Hz.
- Detector : Si(Li) cooled with liquid nitrogen.
- Capacity of liquid nitrogen reservoir : about 20 l. Independence : 10 days.
- Analatycal program capacity : 4 (out of 8 options).
- Probe Type II (analysis of powders, liquids or flat surfaces).

NO 2



SEALED RADIOACTIVE SOURCE

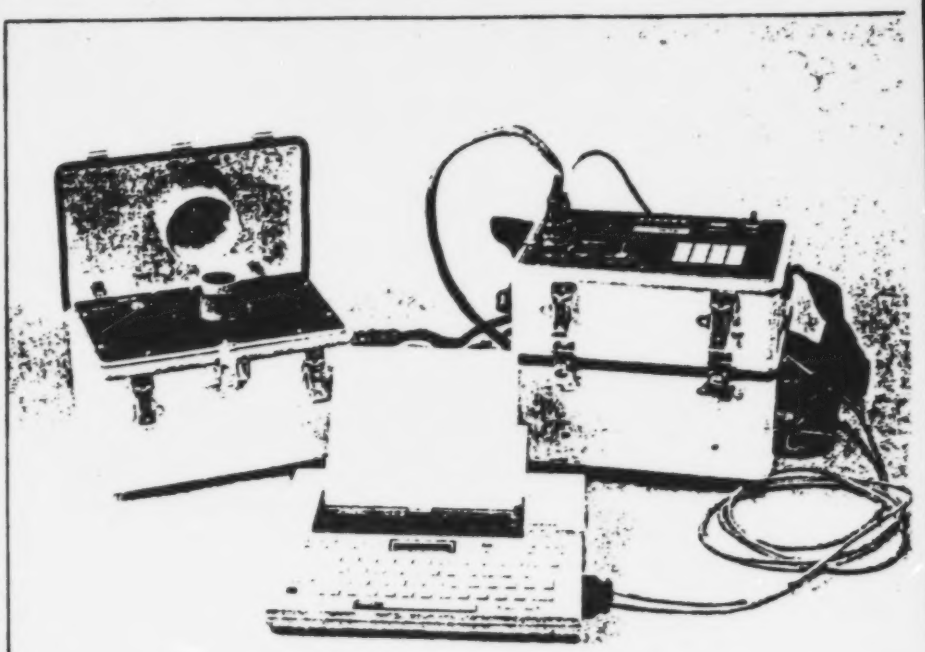
- Fe55, 20 mCi.
- Cd109, 10 mCi.
- Am241, 10 mCi.
- Am241, 100 mCi.

OPTIONS

- Printer.
- 4 supplementary analytical programs.
- Probe with source Am241 of 100 mCi.
- Expendable items (on request):
  Specimen holders for powder or liquids (lots of 10).
  Mylar sheets: 36 μm (powders)
  10 μm (solutions).

SYRANO 3

TRANSPORTABLE APPARATUS



TECHNICAL SPECIFICATIONS

Basic instrument comprising an analysis case with AC power supply 110/220 Volts, 50-60 Hz and a Type IIIa, IIIb or IIIbr probe with a radioactivity shield (for source Am241, 100 mCi).

ANALYZER CASE

- Case dimensions: 310×245×330 mm.
- Weight of the case: 10.5 kg.
- Operating temperature: 0-45°C.
- Display: liquid crystal alphanumeric.
- Keyboard: 12 keys with 4 reserved for program selection.
- Power unit or generator: 110/220 V; 50-60 Hz.
  Consumption: 27 Watts.
- Analatycal program capacity: 4 programs (out of 8 options).

PROBE TYPE IIIa
Only accepts sources of 20 or 10 mCi.

or

PROBE TYPE IIIb
Only accepts sources of 20 or 10 mCi.

or

PROBE TYPE IIIbr
(Radioactivity shield for source Am241 of 100 mCi) at extra cost.

SEALED SOURCES

- Fe55, 20 mCi.
- Cd109, 10 mCi.
- Am241, 10 mCi.
- Am241, 100 mCi.

OPTIONS

- Printer.
- 2nd probe Type IIIa or b with different 10 mCi source, or probe Type IIIb with shield for Am241, 100 mCi.
- 4 supplementary programs.
- Expendable items (on request).
  Specimen holders for powders or liquid (lots of 10).
  Mylar sheets: 36 μm (powder)
  10 μm (solutions).

BRGM

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GÉOLOGIQUES ET MINIÈRES

DÉPARTEMENT ANALYSE

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Guy Raymond

$78,600 mai 87

INTERMETRIX SYSTEMS INC.
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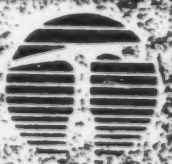

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THÉORIE ET COEFFICIENTS DE CORRECTIONS POUR L'EFFET DE MATRICE (ALGORITHME FONDAMENTAL)

Fundamental Algorithm Between Concentration and Intensity in XRF Analysis

1—Theory

Richard M. Rousseau
Geological Survey of Canada, 601 Booth Street, Ottawa, Canada, K1A OE8

A new formalism is proposed to correct with accuracy the matrix effects in x-ray fluorescence (XRF) analysis. It has been deduced from Sherman's equations and includes a new algorithm between concentration and intensity, theoretically exact, and explicit expressions permitting the calculation of α_{ij} and ρ_{ij} coefficients that correct for absorption and enhancement effects, respectively. In other words, the concept of correction coefficients is established on a solid theoretical basis. In the second part, it will be shown how to adapt this new formalism to practical situations. From an estimate of composition calculated by the Claisse–Quintin algorithm and an appropriate calibration, the new algorithm is used to refine the estimated composition for greater accuracy. This last approach is equivalent to the 'fundamental parameters' method but is presented in a simpler version adaptable to any mini-computer.

INTRODUCTION

Since the birth of quantitative x-ray fluorescence (XRF) analysis, a multitude of empirical, semi-empirical and theoretical methods[1–4] have been proposed to correct for matrix effects and to convert measured intensities (I_i) to concentrations (C_i). Many of these methods suggest various algorithms, relating C_i to I_i, which do not at first sight appear to have a common origin, or to relate to each other. On the other hand, Sherman[5,6] proposed in 1955 a theoretical formalism that is essentially exact and permits the calculations of the x-ray intensity emitted by an element in a specimen of known composition.

The question is, then, is it possible to deduce from Sherman's equations an algorithm that is theoretically exact and that would serve as a common basis to generate all other models proposed to date? Moreover, is there a fundamental algorithm relating C_i to I_i which perfectly corrects for all matrix effects, i.e. absorption and enhancement? The answer to both queries is affirmative, and in addition to presenting this new algorithm for the first time, theoretically exact explicit expressions will be given enabling the calculation of α_{ij} and ρ_{ij} coefficients that correct for absorption and enhancement effects respectively.

It will be shown that this new formalism is very simple, enables the physical concepts underlying Sherman's equations to be clearly illustrated, facilitates the comprehension of phenomena specific to x-ray fluorescence and greatly facilitates the writing of computer programs.

Further, from this new fundamental algorithm can be deduced any other algorithm that has been proposed and is theoretically valid, for example that of Lachance and Traill or of Claisse and Quintin. The new algorithm also permits us to show that certain algorithms are not theoretically valid, for example that of Rasberry and Heinrich. Also, it can serve as a sound theoretical basis for generating new algorithm to meet specific needs.

THEORETICAL BASIS

The basic equations relating x-ray fluorescence intensity from a sample and its composition were derived by Sherman[5,6] and some other authors.[7,8] The expression used to express the intensity of the fluorescent radiation emitted by an element i in a sample containing several other elements j can be written as shown in Table 1. The tertiary x-ray fluorescence intensity will not be considered here because its value is usually very small and would not help in a better understanding of the present approach.

As can be seen in Table 1, the large number of fundamental parameters involved and especially the polychromaticity of the primary beam used to excite the fluorescence make this equation complex and difficult to handle and it has no clear relationship with the physical phenomena involved in XRF analysis. Sherman's equation will therefore be completely rewritten in a manner that will facilitate its use and reval information on the basic rules of matrix effect corrections.

The first parameter needed to calculate the intensity from element i with Eqn (1) is the spectral distribution of the primary radiation. However, there is no analytical expression which can generate any incident spectrum in an essentially exact manner, for any experimental conditions. Also, in the present paper, the measured spectra[9] will be used rather than theoretical descriptions of the x-ray tube output. The integral over λ is here replaced by a finite summation of k values of wavelength intervals $\Delta\lambda_k$ with corresponding measured intensities $I_0(\lambda_k)$:

$$\int_{\lambda_{min}}^{\lambda_{max}} I_0(\lambda)\,d\lambda \rightarrow \sum_{k=\lambda_{min}}^{\lambda_{max}} I_0(\lambda_k)\,\Delta\lambda_k$$

CCC-0049–8246/84/0013–0115$03.00

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Table 1. Sherman's equation and definition of symbols

$$I_i(\lambda_i) = g_i C_i \int_{\lambda_{min}}^{\lambda_{edge\,i}} \frac{\mu_i(\lambda)}{\mu_s'(\lambda) + \mu_s''(\lambda_i)} \left[1 + \sum_j C_j \delta_{ij}(\lambda)\right] I_0(\lambda)\, d\lambda \qquad (1)$$

$$g_i = k_i S \frac{\Omega}{4\pi} \operatorname{cosec} \theta'$$

$$k_i = \frac{r_i - 1}{r_i}\, \omega_i p_i$$

$$\mu_s'(\lambda) = \sum_{i=1}^{N} C_i \mu_i(\lambda) \operatorname{cosec} \theta'$$

$$\mu_s''(\lambda_i) = \sum_{i=1}^{N} C_i \mu_i(\lambda_i) \operatorname{cosec} \theta''$$

$$\delta_{ij}(\lambda) = \frac{D_{ij}}{2} k_i \mu_j(\lambda_i) \frac{\mu_j(\lambda)}{\mu_j(\lambda)} P_{ij}(\lambda)$$

$$P_{ij}(\lambda) = \frac{1}{\mu_s'(\lambda)} \ln\left[1 + \frac{\mu_s'(\lambda)}{\mu_s(\lambda_i)}\right] + \frac{1}{\mu_s''(\lambda_i)} \ln\left[1 + \frac{\mu_s''(\lambda_i)}{\mu_s(\lambda_j)}\right]$$

i	Analyte
j	Any interfering element in the matrix
$I_i(\lambda_i)$	Total counting rate for a line of element i
λ_i	Wavelength of a line of element i
C_i	Weight concentration of element i
λ_{min}	Minimum wavelength of the primary radiation
$\lambda_{edge\,i}$	Wavelength of the considered edge of element i
$I_0(\lambda)\, d\lambda$	Spectral distribution of primary radiation over interval $d\lambda$
$\mu_i(\lambda)$	Mass absorption coefficient of element i for wavelength λ (cm^2/g)
$\mu_s(\lambda)$	Mass absorption coefficient of the specimen for wavelength λ
r_i	Jump ratio of element i for edge of considered line
ω_i	Fluorescence yield for line of element i
p_i	Transition probability for considered line of element i
θ'	Angle between central beam of tube radiation and surface of the specimen
θ''	Take-off angle of measured radiation from specimen
S	Irradiated area of specimen
Ω	Detection solid angle
D_{ij}	Is unity when element j can enhance analyte i, i.e. if $\lambda_k <$ λ edge j and $\lambda_j < \lambda$ edge i; it is zero in all other cases

By doing that, Eqn (1) and the following equations stay essentially the same and permit us to calculate the integral without having to express the intensity $I_0(\lambda)$ in an explicit form.

In the second important step, because of the difficulty in determining the experimental constant g_i, the absolute intensity from element i is expressed as relative x-ray intensity:

$$R_i = \frac{I_i(\lambda_i)}{I_{(i)}(\lambda_i)} \qquad (2)$$

where $I_{(i)}(\lambda_i)$ is the intensity from pure element i. Now, having in mind for a given specimen of N elements:

$$\sum_{i=1}^{N} C_i = 1 \qquad (3)$$

and defining the following variables:

$$\mu_i^* = \mu_i(\lambda_k) \operatorname{cosec} \theta' + \mu_i(\lambda_i) \operatorname{cosec} \theta'' \qquad (4)$$

$$\beta_{ij}(\lambda_k) = \frac{\mu_j^*}{\mu_i^*} - 1 \qquad (5)$$

$$W_i(\lambda_k) = \frac{\mu_i(\lambda_k) I_0(\lambda_k)\, \Delta\lambda_k}{\mu_i^* \left[1 + \sum_j C_j \beta_{ij}(\lambda_k)\right]} \qquad (6)$$

we obtain, after an algebraic manipulation, the 'modified Sherman's equation:'

$$C_i = R_i \frac{\sum_k W_i(\lambda_k) \left[1 + \sum_j C_j \beta_{ij}(\lambda_k)\right]}{\sum_k W_i(\lambda_k) \left[1 + \sum_j C_j \delta_{ij}(\lambda_k)\right]} \qquad (7)$$

In this form, the Sherman equation is already simpler and more revealing. The XRF analyst, instead of calculating the intensity from analyte i as before, may now calculate the concentration of element i from the measured relative intensity R_i, which is corrected for matrix effects by the ratio on the right-hand side. Before going further, the reader can easily guess that the numerator corrects for absorption effects of every element j of the matrix and the denominator for enhancement effects of every element j. All these matrix effects are weighted by the factor W_i, which

takes into account the polychromaticity of the incident spectrum. We shall return to this subject later.

If in Eqn (7) the brackets are removed in both numerator and denominator, and each term is divided by $\sum_k W_i(\lambda_k)$, we obtain finally

$$C_i = R_i \frac{1+\sum_j C_j \alpha_{ij}}{1+\sum_j C_j \rho_{ij}} \tag{8}$$

with

$$\alpha_{ij} = \frac{\sum_k W_i(\lambda_k)\beta_{ij}(\lambda_k)}{\sum_k W_i(\lambda_k)} \tag{9}$$

and

$$\rho_{ij} = \frac{\sum_k W_i(\lambda_k)\delta_{ij}(\lambda_k)}{\sum_k W_i(\lambda_k)} \tag{10}$$

Henceforth, Eqn (8) will be called the 'fundamental algorithm' in this paper and Eqns (9) and (10) will be the fundamental explicit equations used to calculate the coefficients correcting for absorption and enhancement effects, respectively. We shall see why in the next section.

PHYSICAL INTREPRETATION

As it stands, Eqn (8) contains all that is needed to analyse a specimen by XRF and also provides a complete correction for all matrix effects. This relation is perfectly exact since it was deduced from Sherman's equations without involving any approximation in the process of derivation. Also, if one accepts the fundamental nature of the Sherman equations in XRF, it follows that Eqn (8), being derived directly from Sherman's must be recognized as equally fundamental. Thus, Eqn (8) can be considered as the only fundamentally exact algorithm between concentration and intensity in XRF.

The physical meaning of the fundamental algorithm is obvious. To a first approximation, Eqn (8) reveals that the concentration of the analyte i is proportional to its measured relative intensity, i.e. $C_i \approx R_i$, which is multiplied by a ratio correcting for all matrix effects. In fact, the coefficient α_{ij} through the β_{ij} coefficients includes all mass absorption coefficients μ_s (when there is no enhancement) of Sherman's equations. Therefore, we can assume that the α_{ij} coefficient corrects for all absorption effects caused by element j on analyte i and the numerator of the ratio corrects for all absorption effects of the matrix, each element j bringing its contribution to the total correction in a proportion C_j. Note that the concentration of the analyte i does not appear in the ratio because the coefficient β_{ij} expresses each mass absorption coefficient μ_j^* as a ratio to μ_i^* (therefore $\alpha_{ii} = 0$). If the numerator is greater than unity (it could be lower if the matrix is less absorbing than the analyte), the intensity R_i will be increased by a quantity equivalent to that absorbed by the matrix. Briefly, the α_{ij} coefficient corrects for absorption effects and its only acceptable theoretical definition is given by Eqn (9).

Now, if some elements of the matrix are able to enhance the analyte, the corresponding coefficients ρ_{ij} through δ_{ij} will be different from zero and essentially positive. Then, the denominator will be greater than unity and the intensity R_i will be reduced by a quantity equivalent to that caused by the enhancement. Thus, the ρ_{ij} coefficient corrects for enhancement effects and its only acceptable theoretical definition is given by Eqn (10).

Now that we have a better understanding of the fundamental algorithm, let us have a closer look at the α_{ij} and ρ_{ij} expressions. First, let us recall, that in statistics, if with each value x_i is associated a weighting factor $w_i \geq 0$, then the weighted mean $\bar{x}$ is calculated by

$$\bar{x} = \frac{\sum_i w_i x_i}{\sum_i w_i}$$

Eqns (9) and (10) have precisely the form of the equation above! So, by analogy, we can say that α_{ij} and ρ_{ij} are the *weighted means* of all absorption and enhancement effects, respectively, caused by element j on analyte i, when to each wavelength λ_k is given a weight equal to $W_i(\lambda_k)$; but weighted by what, and what is included in the W_i factor?

Equation (6) for the weight factor $W_i(\lambda_k)$ can be seen as the product of two terms:

$$W_i(\lambda_k) = \left[\frac{\mu_i(\lambda_k)}{\mu_i^*} I_0(\lambda_k)\,\Delta\lambda_k\right]\left[\frac{1}{1+\sum_j C_j \beta_{ij}(\lambda_k)}\right]$$

where the first one gives a weight to each value of the incident intensity $I_0(\lambda_k)\,\Delta\lambda_k$. The second term weighs in each binary matrix effect i–j by the total absorption effect of the matrix, which makes physical sense! The weight factor W_i takes in account the polychromaticity of the incident spectrum and in which kind of matrix are the elements i and j.

These considerations about W_i lead to the two following important conclusions:

1. The α_{ij} and ρ_{ij} coefficients are not constants for a binary system i–j and change not only with the concentration of element j but also with the nature and concentration of all other elements in the matrix.
2. The total matrix effect on the analyte i is not equal to the sum of the effects of every element j of the matrix, calculated independently of each other. In other words, each element j contributes to the total matrix effect on the analyte i, but the individual contribution of each element j cannot be isolated and cannot be calculated independently from all other elements of the matrix.

In the light of these conclusions, we can now understand why methods based on the hypothesis that the total matrix effect is equal to the sum of each binary effect i–j were giving results with more or less accuracy.

Table 2. Values of α and ρ coefficients in the fundamental algorithm for a given hypothetical specimen; the concentrations C_i and the calculated relative intensities R_i are given*

Parameter	Na	Mg	Al	Si	P	S	K	Ca	Ti	Cr	Mn	Fe
C_i	3.00	3.00	14.00	55.00	0.50	0.10	2.00	7.00	2.00	0.10	0.30	13.00
R_i	0.0067	0.0093	0.0537	0.1795	0.0009	0.0002	0.0120	0.0521	0.0216	0.0009	0.0029	0.1373

Matrix

Coefficient	Analyte	Na	Mg	Al	Si	P	S	K	Ca	Ti	Cr	Mn	Fe
α	Na	0.0000	0.4652	0.9327	1.5107	2.1840	2.9352	5.9175	7.1608	10.1078	12.8691	14.7831	16.7433
	Mg	9.1414	0.0000	0.3153	0.7041	1.1567	1.6608	3.6528	4.4793	6.4226	7.9871	9.2251	10.4936
	Al	6.1233	6.2799	0.0000	0.2911	0.6296	1.0057	2.4830	3.0919	4.5088	5.3859	6.2633	7.1627
	Si	4.0178	5.5370	7.0867	0.0000	0.2580	0.5439	1.6581	2.1138	3.1594	3.5492	4.1719	4.8106
	P	2.5862	3.6459	4.7562	6.0351	0.0000	0.2232	1.0850	1.4337	2.2212	2.2696	2.7148	3.1719
	S	1.5731	2.3521	3.1693	4.0907	5.1914	0.0000	0.6866	0.9613	1.5716	1.3866	1.7091	2.0406
	K	0.0083	0.3136	0.6361	1.0101	1.4447	1.8971	0.0000	0.1501	0.4694	−0.0267	0.0995	0.2299
	Ca	−0.2411	−0.0113	0.2327	0.5162	0.8441	1.1877	2.4044	0.0000	0.2690	−0.2556	−0.1611	−0.0633
	Ti	−0.5522	−0.4166	−0.2712	−0.1020	0.0922	0.2981	1.0238	1.2828	0.0000	−0.5434	−0.4887	−0.4319
	Cr	−0.4839	−0.3277	−0.1586	−0.0387	0.2633	0.5042	1.3494	1.6549	2.3801	0.0000	−0.0012	0.0060
	Mn	−0.5454	−0.4078	−0.2582	−0.0835	0.1147	0.3285	1.0767	1.3488	1.9930	−0.1078	0.0000	−0.0053
	Fe	−0.5969	−0.4749	−0.3417	−0.1859	0.0099	0.1809	0.8476	1.0914	1.6672	2.3501	−0.1018	−0.0000

Matrix

ρ	Na	0.0000	0.0927	0.1202	0.1345	0.0852	0.1130	0.2184	0.2479	0.2721	0.0187	0.0175	0.0167
	Mg	0.0000	0.0000	0.1282	0.1434	0.0903	0.1203	0.2327	0.2636	0.2885	0.0198	0.0185	0.0176
	Al	0.0000	0.0000	0.0000	0.1497	0.0936	0.1256	0.2455	0.2784	0.3049	0.0211	0.0196	0.0187
	Si	0.0000	0.0000	0.0000	0.0000	0.0926	0.1243	0.2439	0.2769	0.3040	0.0211	0.0196	0.0187
	P	0.0000	0.0000	0.0000	0.0000	0.0000	0.1144	0.2224	0.2528	0.2782	0.0192	0.0179	0.0172
	S	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.2344	0.2664	0.2931	0.0203	0.0189	0.0181
	K	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.3128	0.3469	0.0250	0.0233	0.0222
	Ca	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.3619	0.0268	0.0250	0.0239
	Ti	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0312	0.0294	0.0282
	Cr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.5896
	Mn	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	Fe	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

* Specimen, ROU-1; geometry 64,35°; tube, Cr, 45 kV (C.P.).

In order to illustrate the quantitative aspects of α_{ij} and ρ_{ij} coefficients, Table 2 gives all the values needed to correct adequately for matrix effects in a given specimen. Note that these values are valid only for this specimen since they depend on the matrix composition. Any other specimen with the same series of elements, but in different proportions, will need a new set of values to correct exactly for matrix effects.

APPLICATION EXAMPLES OF THE FUNDAMENTAL ALGORITHM

One of the consequences of the fundamental algorithm is that any other proposed algorithm should be equivalent to the fundamental one to be valid. Otherwise, the proposed algorithm will not be in agreement with the theory and its existence would be seriously doubtful.

To illustrate this fact, the three most popular algorithms are considered, i.e. those of Lachance and Traill (L–T),[1] of Rasberry and Heinrich (R–H)[2] and of Claisse and Quintin (C–Q).[10] The fundamental algorithm can be written in the form

$$\frac{C_i}{R_i} = \frac{1+x}{1+y} \tag{11}$$

where

$$x = \sum_i C_i \alpha_{ij} \tag{12}$$

and

$$y = \sum_i C_i \rho_{ij} \tag{13}$$

The L–T algorithm can easily be deduced from Eqn (11) by adding (1 − 1) to the right-hand side term. We obtain

$$\frac{C_i}{R_i} = 1 - 1 + \frac{1+x}{1+y} = 1 + \frac{x-y}{1+y} \tag{14}$$

and replacing x and y by their respective values, we obtain

$$\frac{C_i}{R_i} = 1 + \sum_i C_i a_{ij} \tag{15}$$

where

$$a_{ij} = \frac{\alpha_{ij} - \rho_{ij}}{1 + \sum_i C_i \rho_{ij}} \tag{16}$$

which is the well known L–T relation and where all the matrix effects, absorption and enhancement, are expressed by the one and only coefficient a_{ij}. Thus, the form of the L–T relation is theoretically right and its

use is recommended mainly to analyse geological materials in the form of fused discs.

Concerning the α_{ij} coefficient, Lachance and Traill proposed the following expression (using the present symbolism):

$$\alpha_{ij} = \beta_{ij} = \frac{\mu_j^*}{\mu_i^*} - 1$$

which can be deduced from Eqn (16) when two severe restrictions are imposed: (a) if there is no enhancement ($\rho_{ij} = 0$) in the specimen; and (b) if the polychromatic incident beam is considered as equivalent to a monochromatic one. In practical situations these two limitations are rarely met. Equation (16) is then more general and fits better with today's physical reality.

To obtain the R–H model, Eqn (14) can be rewritten as

$$\frac{C_i}{R_i} = 1 + \frac{x}{1+y} - \frac{y}{1+y}$$

Using Eqns (12) and (13), the theoretical equivalent of the R–H model is given as follows:

$$\frac{C_i}{R_i} = 1 + \sum_j A_{ij} C_j + \sum_i \frac{B_{ij}}{1 + \sum_i C_j \rho_{ij}} C_i \qquad (17)$$

where

$$A_{ij} = \frac{\alpha_{ij}}{1 + \sum_i C_j \rho_{ij}} \qquad (18)$$

and

$$B_{ij} = -\rho_{ij} \qquad (19)$$

For the R–H model to be in agreement with the theoretical model, one must assume that

$$C_i = \sum_j C_j \rho_{ij}$$

which is a very gross approximation, as is shown by the data in Table 2. Rasberry and Heinrich proposed also that when element j enhances the analyte i, coefficient $B_{ij} \neq 0$ and the corresponding A_{ij} is zero That is false, as can be seen from Eqns (18) and (19). Further, we have verified that practical analysis of complex systems with the R–H model give results that are not as accurate as they might be. Thus, for all these reasons, the use of the R–H model is not recommended and we even contest its existence, as it is not theoretically valid.

The verification of the C–Q model is effected as follows. Rewriting Eqn (11) in the form

$$\frac{C_i}{R_i} = (1+x)\left(\frac{1}{1+y}\right) = (1+x)\left(1 - 1 + \frac{1}{1+y}\right)$$

$$= (1+x)\left(1 - \frac{y}{1+y}\right)$$

and rearranging:

$$\frac{C_i}{R_i} = 1 + x - \frac{y}{1+y} - \frac{xy}{1+y}$$

Again, replacing x and y by their respective values, one obtains

$$\frac{C_i}{R_i} = 1 + \sum_j C_j a_{ij} + \sum_i C_i^2 a_{iij} + \sum_j \sum_{k>j} C_j C_k a_{ijk} \qquad (20)$$

where

$$a_{ij} = \alpha_{ij} - \frac{\rho_{ij}}{1 + \sum_j C_j \rho_{ij}} \qquad (21)$$

$$a_{iij} = -\frac{\alpha_{ij}\rho_{ij}}{1 + \sum_j C_j \rho_{ij}} \qquad (22)$$

and

$$a_{ijk} = -\frac{\alpha_{ij}\rho_{ik} + \alpha_{ik}\rho_{ij}}{1 + \sum_j C_j \rho_{ij}} \qquad (23)$$

The theoretical model thus obtained is perfectly in agreement with the one proposed by Claisse and Quintin and can be recommended for the analysis of any material in which strong matrix effect variations occur.

We find, for the coefficient a_{ij}, the same relation as proposed by Claisse and Quintin (for non-enhancement cases) if we assume that

$$W_i(\lambda_k) = \frac{\mu_i}{\mu_i^*} I_0(\lambda_k)\, \Delta\lambda_k$$

which necessitate that each binary effect i–j is *not* weighted by the matrix composition. As we now know, this assumption is false and therefore the relations described above are more appropriate to the XRF reality than those proposed by Claisse and Quintin. One surprising conclusion from Eqns (22) and (23) is that a_{iij} and a_{ijk} become zero if there is no enhancement ($\rho_{ij} = 0$). Thus the second-order terms disappear and the C–Q relation becomes the L–T relation.

For the sake of brevity, it is not possible to compare here all algorithms proposed in the literature with the fundamental one. However, one thing is certain: if one proposed algorithm is not equivalent to the fundamental one, its form cannot be *theoretically* right and its application to practical situations will give more or less accurate results.

In the meantime, from the three examples given, one important thing to keep in mind is that the new formalism not only permits a test of the theoretical validity of any proposed algorithm, but also gives for each coefficient an explicit expression, in terms of fundamental parameters only. It then becomes possible to compare coefficients from one algorithm with those from another.

Another useful feature of the new algorithm is that it provides a solid theoretical foundation upon which it is possible to base the derivation of other algorithms to meet specific needs. Also, because the fundamental algorithm clearly resolves the expressions governing absorption and enhancement, it facilitates the writing of computer programs.

CONCLUSION

A fundamental algorithm between C_i and R_i has been deduced from Sherman's equations without involving any approximation in so doing. Its explicit expression is then essentially exact and corrects completely for all

matrix effects affecting the intensity R_i from analyte i in a given specimen.

The coefficients α_{ij} and ρ_{ij} correct for absorption and enhancement effects, respectively. They are calculated from fully explicit equations, in terms of fundamental parameters only. These equations are proposed as definitions of coefficients correcting for matrix effects in XRF analysis and permit the establishment of a sound theoretical basis for the concept of correcting coefficents. There would therefore be no justification for further use of empirical or semi-empirical coefficients in the literature or in analytical practice.

The rewriting of Sherman's equations in the proposed form enables one to illustrate clearly and simply all the physical concepts hidden behind so many parameters. In particular, it facilitates the understanding that α_{ij} and ρ_{ij} are merely the averages of all absorption and enhancement effects for all wavelengths when to each one is associated a weight factor W_i.

Another useful aspect of the new formalism is that it provides a clear indication of the importance of the matrix effect of every element j on the analyte i and of the contribution of each element j to the total matrix effect. In other words, one can quantify with accuracy all matrix effects caused by element j on analyte i and thus retain a maximum physical meaning. From a theoretical point of view, it also discredits the all-too-common assumption that the correction for total matrix effect is equal to the sum of the binary corrections, calculated independently from each other.

In conclusion, the new formalism is a powerful, accurate and prolific tool used in calculating such varied parameters as the basic, hybrid and modified α coefficients after the terminology of Lachance,[11] applied to many kinds of specimens (alloys, rock, ore, cement, etc.), to check the accuracy of a given algorithm when applied to a specific series of specimens, to calculate the coefficient correcting for volatile products lost during the preparation of fused discs, and so on. Briefly, its use can be only beneficial to the work of any XRF analyst.

Naturally, this new formalism would have less interest if it were not easily adapted to practical analytical situations. This is the subject of Part 2.

REFERENCES

1. G. R. Lachance and R. J. Traill, 11, 43 (1966).
2. S. D. Rasberry and K. F. J. Heinrich, 46, 81 (1974).
3. J. W. Criss and L. S. Birks, *Anal. Chem.*, 40, 1080 (1968).
4. R. Jenkins, *Adv. X-Ray Anal.* 22, 281 (1979).
5. J. Sherman, *Spectrochim. Acta.* 7, 283 (1955).
6. J. Sherman, *Spectrochim. Acta* 15, 466 (1959).
7. T. Shiraiwa and N. Fujino, *Jpn. J. Appl. Phys.* 5, 886 (1966).
8. R. P. Garner and J. M. Doster, *Adv. X-Ray Anal.* 22, 343 (1979).
9. J. V. Gilfrich and L. S. Birks, *Anal. Chem.* 40, 1077 (1968).
10. F. Claisse and M. Quintin, *Can. Spectrosc.* 12, 129 (1967).
11. G. R. Lachance, *X-Ray Spectr.* 8, 190 (1979).

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Fundamental Algorithm Between Concentration and Intensity in XRF Analysis

2—Practical Application*

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In Part 1, a new formalism was proposed to correct with accuracy the matrix effects in XRF analysis. In this paper it is shown how to adapt this new formalism to practical situations. From an estimate of composition calculated by the Claisse–Quintin algorithm and an appropriate calibration, the new algorithm is used to refine the estimated composition for greater accuracy. This last approach is equivalent to the 'fundamental parameters' method but is presented in a simpler version adaptable to any mini-computer.

INTRODUCTION

In Part 1, it was shown that the fundamental algorithm

$$C_i = R_i \frac{1+\sum_j C_j \alpha_{ij}}{1+\sum_j C_j \rho_{ij}} \quad (1)$$

is essentially exact and corrects perfectly all the matrix effects on the condition that the composition of the specimen is known, as a preliminary, since the α_{ij} and ρ_{ij} coefficients are functions of this composition. However, this is precisely what is being sought and it is obvious that it is not known at the starting point. Rigorously, an iterative process could be applied to the fundamental algorithm where the α_{ij} and ρ_{ij} coefficients would participate in the process as variables of the composition and not as constants. However, this procedure would be exactly the same as the one used in the 'fundamental parameters' method,[1,2] thus suffering from the same weaknesses (to which we shall return later), which is precisely what we want to avoid. Therefore, to solve that problem, in a first step an estimated composition is calculated by iterations using the Claisse–Quintin (C–Q) equation:[3]

$$C_i = R_i\left[1+\sum_j C_j(a_{ij}+a_{ijj}C_M)+\sum_j\sum_{k>j} C_jC_k a_{ijk}\right] \quad (2)$$

with previously computed influence coefficients. This equation is written in a slightly different form to take in account the last suggestions of Lachance and Claisse[4] and where C_M is the concentration of the matrix (sum of all the elements except i). From this estimated composition, the α_{ij} and ρ_{ij} coefficients are calculated once and once only with Eqns (9) and (10) from Part 1. Then, knowing all the α_{ij} and ρ_{ij} coefficients for the specimen, a refined estimate of composition is obtained by applying an iterative process to the fundamental algorithm. It should be noted that contrary to the fundamental parameters method, no iteration is applied to the Sherman equation itself in this approach. This has the effect of avoiding all the convergence problems, of reducing substantially the calculation time and of simplifying the procedure.

Commensurate with the application of this new theoretical formalism is the need to adapt to experimental reality by an appropriate calibration, it being well known that no theory accounts for all experimental variables. Therefore, a simple and precise method for calibration is presented.

COMPUTATION OF INFLUENCE COEFFICIENTS IN THE C–Q EQUATION

In practical situations, the corrections for matrix effects with the C–Q equation will be easier if the influence coefficients are considered as constants instead of values which vary with the composition [as defined by Eqns (21), (22) and (23) from Part 1]. In other words, we do the approximation that each binary effect i–j is independent of the rest of the matrix. Of course, this approximation introduces a slight error but the C–Q equation is still accurate enough to permit the calculation of a very good estimate of composition. As we shall see later, the relative error introduced by this approximation is of order of 0.4%.

In the C–Q equation, there are three main methods for determining the constant influence coefficients:

1. The influence coefficients could be determined experimentally from binary standards, but the preparation and measurement of an adequate number of reliable standards in tedious and can easily yield values that are often more or less accurate and have no physical meaning.
2. They could be determined by regression analysis from a set of complex standards. This statistical method is questionable because it is sensitive for

* For Part 1, see p. 115.

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errors in the data, the regression may give large errors on coefficients and they should be applied to unknowns that belong to the group of standards only, otherwise the calculated concentrations may be wrong. Further, the end result is often an overtaxing of the data, which leads to a set of numbers with little or no physical meaning and that are related strictly to intensities measured. A good example of this 'poor' method is given by Criss and Birks.[1]

3. An easier and much more practical method is to compute theoretical coefficients for any combination of elements and any experimental conditions, as described by Rousseau and Claisse.[5] Let us recall here briefly the essential equations in their approach. If for a ternary system (C_i, C_j, C_k) the variable $F_i(C_i, C_j, C_k)$ is defined by

$$F_i(C_i, C_j, C_k) = \frac{1}{C_i}\left(\frac{C_i}{R_i} - 1\right) \tag{3}$$

where the ratio C_i/R_i is given by Eqn (7) from Part 1, the different coefficients are then calculated using the relationships

$$a_{ij} = \tfrac{1}{2}[-F_i(0.2, 0.8, 0) + 4F_i(0.8, 0.2, 0)] \tag{4}$$

$$a_{iij} = \tfrac{3}{2}[F_i(0.2, 0.8, 0) - F_i(0.8, 0.2, 0)] \tag{5}$$

$$a_{ijk} = \tfrac{20}{3}[F_i(0.3, 0.35, 0.35) - F_i(0.3, 0.7, 0) - F_i(0.3, 0, 0.7)] \tag{6}$$

These coefficients have to be calculated once only for a given ternary system i–j–k, are valid for the whole range of compositions (C_i, C_j, C_k), in any kind of matrix and can be stored in computer memory for later use. An example of influence coefficients when iron is the analyte is given in Table 1.

In the fundamental parameters method, Criss[6] suggests using a series of measured and theoretical intensities, covering the whole range of concentrations for each analyte and by a regression analysis, calculate all the needed coefficients in a limited C–Q equation where the a_{ijk} coefficients are zero. With many precautions, there is no doubt that this method gives representative coefficients, except that the procedure is long, complex and not exempted from all possible errors cited above. Further, for many elements the a_{ijk} coefficient is far from zero and cannot be neglected. The proposed method is simpler and as accurate if the calibration procedure suggested in the next section is followed.

CALIBRATION

The calibration step is the link which permits the theory to be correlated with experimental reality. To paraphrase Criss:[6] 'An adjustment process is essential in using any kind of theory for accurate analysis, because no theory alone will ever be able to model all instrumental responses as accurately as needed in all cases.' Another problem is the difficulty (and sometimes the impossibility) of obtaining all the pure element specimens necessary for the analysis of a given specimen. To overcome these two obstacles simultaneously the following calibration procedure from a set of complex standards containing all the elements to be determined is suggested. Recalling that the relative intensity

$$R_i = \frac{I_i}{I_{(i)}} \tag{7}$$

where I_i is the net intensity from analyte i and $I(i)$ the net intensity from pure analyte i, the C–Q equation can be written in the form

$$I_i = I_{(i)} \frac{C_i}{\left[1 + \sum_i C_i(a_{ij} + a_{iij}C_M) + \sum_j \sum_k C_j C_k a_{ijk}\right]} \tag{8}$$

which may be considered as the equation of a straight line, passing through the origin, of general form

$$Y_i = m_i X_i \tag{9}$$

and illustrated in Fig. 1.

The intensity $I_{(i)}$ emitted by pure analyte i is then the slope (m_i) of the calibration graph and consequently is determined from the measurement of all complex standards containing element i, without the need to measure the intensity $I_{(i)}$ itself. Since the value

Table 1. Influence coefficients for use in Claisse–Quintin equation (elemental systems)*

Parameter	Analyte	Matrix Na	Mg	Al	Si	P	S	K	Ca	Ti	Cr	Mn	Fe
aij		−0.5586	−0.4261	−0.2820	−0.1143	0.0741	0.2772	0.9789	1.2330	1.8293	2.5307	−0.1026	0.0000
aiij		−0.0361	−0.0497	−0.0642	−0.0804	−0.0979	−0.1155	−0.1687	−0.1852	−0.2196	−0.2515	0.0000	0.0000
aijk	Na	0.0000											
	Mg	0.0005											
	Al	0.0018	0.0004										
	Si	0.0038	0.0015	0.0004									
	P	0.0063	0.0032	0.0014	0.0003								
	S	0.0089	0.0053	0.0028	0.0011	0.0003							
	K	0.0171	0.0120	0.0082	0.0052	0.0030	0.0015						
	Ca	0.0196	0.0142	0.0100	0.0067	0.0042	0.0024	0.0001					
	Ti	0.0245	0.0186	0.0139	0.0100	0.0069	0.0046	0.0009	0.0004				
	Cr	0.0291	0.0227	0.0176	0.0133	0.0097	0.0070	0.0021	0.0013	0.0003			
	Mn	0.0361	0.0497	0.0638	0.0782	0.0952	0.1107	0.1537	0.1661	0.1902	0.2123		
	Fe	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	

* Analyte, Fe; target, Cr, 45 kv (C.P.); geometry, 64,36°.

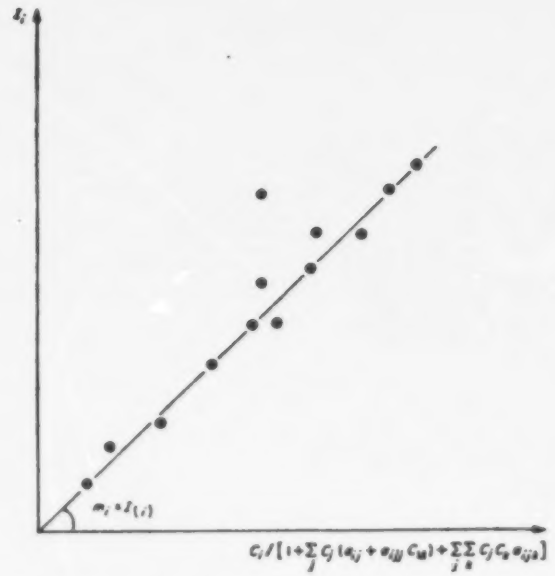

Figure 1. Calibration graph whereby influence coefficients are used to correct for matrix effects for each analyte in the standards and linearize the I_i versus $C_i/(1+\cdots)$ relation with a slope $I_{(i)}$. I_i = measured net intensity from analyte i in each standard; C_i = concentration of analyte i in the standard; m_i or $I_{(i)}$ = calibration slope of analyte i.

for each $I_{(i)}$ is based on data from all the standards on hand, this is likely to be more reliable than that obtained on a single specimen of the pure analyte. If in any manner the intensity $I_{(i)}$ is measured, the slope values calculated from all the other standards could be slightly different because the m_i value takes into account precisely all the imperfections of the theory. Another practical advantage of this procedure compared with the regression techniques is that anomalies, such as single data points that diverge from the calibration graph by more than the reproducibility expected, clearly stand out and facilitate tracing of any error. The unknowns to be analysed do not have to be similar to the standards used for the calibration since the slope m_i depends only on the physical properties of the element i and on the experimental conditions, not on its concentration.

Traill and Lachance[7] and De Jongh[8] have proposed similar methods of calibration but without assimilating the intensity $I_{(i)}$ to the slope of the calibration graph, which has the above-mentioned advantages.

The first step of the calibration permits the calculation of a first estimate of composition. A refined estimate of composition is obtained in applying the same calibration process, but this time to the fundamental algorithm. Using the same standards and the same measured intensities, a new slope m_i' is calculated with the equation

$$I_i = m_i' \frac{C_i}{\dfrac{1+\sum_j C_j\alpha_{ij}}{1+\sum_j C_j\rho_{ij}}} \qquad (10)$$

where each α_{ij} and ρ_{ij} coefficients have been calculated once only for each standard with Eqns (9) and (10) from Part 1.

These two important steps have to be repeated for every element to be determined. Note that the two sets of slopes m_i and m_i' have to be determined once only, provided that the same elements are determined in the same experimental conditions.

ANALYSIS OF UNKNOWNS

After all the intensities emitted by the unknown have been measure, a first estimate of composition is calculated by applying an iterative process to the C–Q equation:

$$C_i = \frac{I_i}{m_i}\left[1+\sum_j C_j(a_{ij}+a_{ijj}C_{ij})+\sum_j\sum_k C_jC_k a_{ijk}\right] \qquad (11)$$

where all the influence coefficients and the set of slopes m_i have been previously stored in the computer memory. Note that the analyst has the opportunity to stop the calculation of composition after this first step if he wants a fast analysis without making fundamental parameters refinements. The average relative error introduced by the model itself (excluding the specimen preparation errors, instrumentation errors, statistical counts errors, etc.) is of the order of 0.4%.

Using this estimated composition, each α_{ij} and ρ_{ij} coefficients are calculated from Eqns (9) and (10) from Part 1 once only. No iteration is applied to these fundamental equations, which reduces the calculation time and avoids all the pitfalls of the fundamental parameters method. Now, with these coefficients used as constants and the second set of slopes m_i' (already stored in computer memory), a refined composition is calculated by applying an iterative process to the fundamental algorithm:

$$C_i = \frac{I_i}{m_i'}\frac{1+\sum_j C_j\alpha_{ij}}{1+\sum_j C_j\rho_{ij}} \qquad (12)$$

At this point, the model alone introduces an average relative error of 0.1% only, four times less than the former one.

As a numerical example, Table 2 presents a series of 12 hypothetical specimens containing 12 elements. The true composition is compared with the estimated and refined composition. All relative intensities have been calculated by Sherman's equations instead of being measured to illustrate the error introduced by each model alone, excluding all the experimental errors. Further, each composition chosen is not realistic. They have been selected because they present very strong matrix effect variations and permit one to visualize how accurate each model succeeds in correcting for them.

The fact of having simplified each step of the method, of course, makes its application simpler but also reduce considerably the time required to calculate the composition of each specimen. It has been observed that the calculation of the composition of a

Table 2. The true composition of hypothetical specimens is compared with the one calculated by the Claisse–Quintin equation and to the one calculated by the fundamental algorithm; relative intensities have been calculated by Sherman's equations

Sample	Na	Mg	Al	Si	P	S	K	Ca	Ti	Cr	Mn	Fe	Total
1	5.00	1.00	15.00	60.00	0.10	0.10	5.00	5.00	3.00	0.70	0.10	5.00	100.00
	5.01	1.01	15.14	60.12	0.11	0.08	5.02	5.00	2.99	0.70	0.10	5.00	100.29
	5.00	1.00	15.01	60.01	0.11	0.08	5.01	5.00	3.00	0.70	0.10	5.00	100.02
2	2.00	25.00	0.10	60.00	0.50	0.10	3.00	3.00	0.50	0.30	0.50	5.00	100.00
	2.02	25.10	0.11	60.09	0.52	0.08	3.00	3.00	0.50	0.30	0.50	5.01	100.23
	2.01	25.02	0.11	60.03	0.52	0.08	3.00	3.00	0.50	0.30	0.50	5.00	100.06
3	0.50	2.00	15.00	75.00	1.00	0.10	1.30	2.00	0.50	0.50	0.10	2.00	100.00
	0.51	2.03	15.30	75.72	1.03	0.09	1.31	2.00	0.50	0.50	0.10	2.00	101.10
	0.51	2.01	15.04	75.14	1.03	0.09	1.31	2.00	0.50	0.50	0.10	2.00	100.23
4	0.50	20.00	0.50	50.00	0.10	0.50	0.90	0.50	4.00	1.00	2.00	20.00	100.00
	0.50	20.04	0.52	50.06	0.11	0.52	0.90	0.50	4.00	1.02	2.00	20.00	100.19
	0.50	20.01	0.52	50.02	0.11	0.52	0.90	0.50	4.00	1.00	2.00	19.99	100.08
5	0.10	2.00	1.00	50.00	1.00	0.10	0.10	45.00	0.10	0.20	0.10	0.30	100.00
	0.08	2.02	1.00	49.83	1.02	0.10	0.10	45.02	0.11	0.19	0.09	0.30	99.87
	0.08	2.01	0.99	49.95	1.02	0.10	0.10	44.99	0.11	0.19	0.09	0.30	99.92
6	3.00	15.00	10.00	65.00	0.40	1.00	1.50	0.50	0.10	1.00	0.50	2.00	100.00
	3.00	15.00	10.15	65.23	0.43	0.98	1.51	0.50	0.10	1.00	0.50	2.00	100.40
	3.01	15.02	10.01	65.05	0.43	0.98	1.51	0.50	0.10	1.00	0.50	2.00	100.10
7	1.50	0.50	15.00	70.00	1.50	0.20	7.50	0.80	0.50	1.00	1.01	0.50	100.00
	1.50	0.50	15.26	70.52	1.52	0.18	7.51	0.81	0.49	1.00	1.01	0.50	100.81
	1.49	0.49	15.02	70.05	1.51	0.18	7.49	0.81	0.50	1.00	1.01	0.50	100.06
8	0.10	1.00	1.00	70.00	0.10	0.10	0.10	25.00	0.10	0.10	2.00	0.40	100.00
	0.11	1.05	1.06	70.21	0.11	0.12	0.10	25.04	0.10	0.10	1.99	0.40	100.39
	0.10	1.01	1.01	70.08	0.11	0.12	0.10	25.02	0.10	0.10	1.99	0.40	100.15
9	8.00	1.00	10.00	70.00	0.50	0.10	2.00	0.40	2.50	0.50	0.50	4.50	100.00
	8.02	1.02	10.22	70.48	0.49	0.09	2.01	0.39	2.49	0.50	0.50	4.50	100.72
	8.00	1.01	10.01	70.04	0.49	0.09	2.00	0.39	2.50	0.50	0.50	4.50	100.04
10	0.10	30.00	20.00	45.00	0.10	0.10	0.10	2.00	0.10	1.00	0.50	1.00	100.00
	0.09	29.65	19.85	44.68	0.12	0.08	0.10	1.99	0.10	1.01	0.50	1.01	99.18
	0.09	29.95	19.96	44.93	0.12	0.08	0.10	2.00	0.10	1.00	0.50	1.00	99.83
11	1.00	6.00	1.00	75.00	0.20	0.10	0.70	10.00	4.00	0.20	1.00	0.80	100.00
	1.02	6.21	1.06	75.60	0.18	0.09	0.70	10.02	3.98	0.20	1.00	0.81	100.86
	0.99	6.00	1.01	75.04	0.18	0.09	0.70	10.00	4.00	0.20	1.00	0.80	100.00
12	0.20	20.00	0.50	35.00	0.10	0.10	1.00	30.00	1.00	0.10	2.00	10.00	100.00
	0.20	19.88	0.48	34.82	0.09	0.10	1.02	30.00	1.00	0.10	1.99	10.01	99.69
	0.21	19.98	0.48	34.98	0.09	0.09	1.01	29.99	1.00	0.10	2.00	10.00	99.92

specimen containing 12 elements takes less than 5 s. This means that an on-line mini-computer will be largely able to process unknowns as fast as they are measured. Considering the core requirements, the maximum amount of memory required for the execution of the program is 22K words, which means that it can be run by any mini- or micro-computer.

CONCLUSION

An accurate XRF analysis method combining theoretical influence coefficients and fundamental parameters calculations has been proposed. The C–Q equation is suggested for calculating a first estimate of composition, which is then used to calculate the α_{ij} and β_{ij} coefficients in the fundamental algorithm once and once only per specimen. After an appropriate calibration, an iterative process is applied to the fundamental algorithm to obtain a refined estimate of composition. The relative error introduced by the model itself is in order of only 0.1%.

Commensurate with the application of this new theoretical formalism is the need to adapt to experimental reality by an appropriate calibration, it being well known that no theory accounts for all experimental variables. Therefore, a simple and precise method for calibration offering a number of practical advantages is presented, namely:

1. It is not necessary to measure intensities $I_{(i)}$ emitted by pure analytes (which may be difficult or impossible to obtain and are likely to present sensitivity problems). The value of $I_{(i)}$ is determined directly from the slope of the calibration graph.
2. The value for each $I_{(i)}$ is based on data from all the standards on hand. This is likely to be more reliable than that obtained on a single specimen of the pure analyte. Calibration standards do not have to be similar to unknown specimens.
3. It provides an effective means of compensating for slight shortcomings in both theory and technique.
4. Anomalies, such as single data points that diverge from the calibration graph by more than the reproducibility expected, clearly stand out and facilitate tracing of any error.

It should be noted that contrary to the fundamental parameters method, no iteration is applied to the

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PAINLESS XRF ANALYSIS USING NEW GENERATION COMPUTER PROGRAMS

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ABSTRACT

A new computer program, named CiROU, has been written to determine the chemical composition of homogeneous samples analyzed by X-ray fluorescence spectrometry (XRF). It uses the fundamental algorithm to convert measured intensities into concentrations and to correct for matrix effects and runs on any IBM-PC/XT/AT, PS/2 or compatible computer.

The program is very easy to use mainly because it is a step-by-step guide to the routine process of analyzing specimens by XRF and because a user friendly interface makes up a main menu bar containing six major options, which provide several other options inside a pull-down window system.

The program is applicable to specimens of any composition with the utmost accuracy that can be obtained from the fundamental-parameters method. It's unique calibration procedure still adds to the accuracy by eliminating the bias between theory and reality.

The program is a complete "off-line" program allowing to perform all the steps of an XRF analysis: calculation of theoretical influence coefficients, calibration, reading of measured intensities, calculation of net intensities and concentrations of unknowns, print-out of analytical reports and data transmission to or from an external computer.

INTRODUCTION

For the last 30 years, X-Ray Fluorescence (XRF) analysis has undergone a spectacular evolution from all points of view. Today, WDS spectrometers supplied by the four major companies (ARL, PHILIPS, RIGAKU, SIEMENS) are completely computer controlled, making them very flexible. High tension generators are more compact, more stable and more powerful. Dual anode x-ray tubes are now available. New reliable sample changers can automatically read up to 72 specimens in any order. The new generation of spectrometers is very sensitive, particularly for the determination of trace ele-

ments, affording better detection limits. They can detect ultra light elements (B, C, F, etc.) mainly because of the new multilayer synthetic crystals. To operate these new spectrometers, cheaper more powerful computers are now available. Control and qualitative software distributed with these are of a high quality.

Sample preparation is still a problem but is improving every year. Quantitative methods to convert measured intensities into concentrations are no longer lacking as shown in the former paper[1]. Algorithms have been proposed that effectively cover a much greater composition range with greater accuracy. New calibration methodology to adapt theory to the real world of XRF analysis, as explained in the former paper, as well as the availability of standards of increasingly well defined and diverse compositions give greater precision and accuracy.

But aside from this impressive list of features, there is one place where improvement can still take place: it is the software used for quantitative analysis. That is why the XRF analyst who developed the methods for XRF analysis[2,3,4,5] decided to write, in collaboration with other analysts, the matching computer program. Three years ago, a team of XRF analysts then started to develop a computer program which was exclusively designed around XRF analysis and written by focusing on the point of view of the XRF analyst. The program was not written by programmers, but by XRF analysts from their day to day experience, wishing to supply a tool which is a step-by-step guide to the "nuts and bolts" process of analyzing specimens by XRF and taking advantage of the most recent developments regarding mathematical models and methods of XRF analysis. The final product must be adapted to the needs of XRF analysts and be a professional product, not an "amateur" one.

It is the purpose of this paper to share the experience thus obtained and to inform the XRF analysis community of the potential of a new generation of XRF programs to analyze any kind of material.

OBJECTIVES OF THE PROGRAM

With the high technology of new spectrometers, comprehensive software packages must now be available which can be interfaced with virtually any XRF spectrometer via a mini or micro computer and by using the measured intensities they can apply the most advanced procedures to suit the analytical requirements of different users.

In order to make the program accessible to a as large as possible number of users, it must run on the most popular computer, the least expensive but at the same time it must also offer high speed calculations and high accuracy. Therefore, the program runs on any IBM-PC, -XT, -AT, PS/2 or compatible computer with 640 KB of memory, a 360 KB floppy disk drive, a hard disk drive and a math coprocessor (8087/80287/80387). A PC/MS-DOS operating system is also needed. If the spectrometer is controlled by an IBM-non-compatible computer, a communication package, like PROCOMM V2.42[6], can be used to transfer the measured intensity files.

The fundamental-parameters method associated with the theoretical multi-element influence coefficient concept is certainly the most powerful and accurate method known today to convert measured intensities into concentrations. And it seems that it will become the most popular one in the near future, especially with computer performance increasing all the

time with decreasing cost. Empirical and approximate methods are becoming obsolete. That is why the program uses the fundamental algorithm as developed by Rousseau[2] to calculate the sample compositions. The calibration procedure used is the one proposed in the former paper.

Which features should an XRF analyst expect to find in a modern program to make his or her work easier and to produce accurate results ? Most importantly, the program must be easy to use, with plenty of features designed to avoid human errors. The program should be accessible to any non-expert by being a step-by-step guide to routine analyses by XRF and by automatically taking care of all complex aspects of the theory. To really make the program easy to use, it should be written for the analyst having little or no experience with the fundamental-parameters approach. Any new user should be productive after a few hours of training only. The documentation should not be really necessary because the number of commands to learn and remember are minimized. Keystrokes should be few and intuitive.

The program should make the analyst's work more accurate, more productive, and more enjoyable. It should be a highly flexible program that also automatically performs many of the more trivial and repetitive tasks. All of the tedious calculations, and parameter entries should be eliminated to increase the efficiency. Each data entry should be saved by the program in order to minimize the number of keystrokes. The time of the XRF analyst is then conserved for the more demanding parts of the analysis, not wasted on repetitive entries of information that the computer already has in memory. You should not have to enter or remember a single code or parameter. Keyboard entries should basically be limited to filenames. With so much of the work done for you, how to use the program should be much faster and easier to learn.

MAIN MENU

All of the above objectives of the program were reached mainly because of the user interface utilized. Older user interfaces employed a menu system, where the user was continually presented with lists of choices requiring that he or she type-in a letter or number to make a selection. Such menus promote human error entries. Furthermore, the result of such a choice was often simply another menu, then another one, and so on. In the end, it was easy to lose the searched place in the menu structure, and to forget how to get from one menu to another.

The pull-down menu concept is a simple improvement: a menu only appears when the user points to the menu title (usually one of a number of choices across the top of the screen). The menu "pulls down" over a portion of the existing screen and allows the user to make a choice from the menu items. After the choice is made, the menu disappears, restoring the initial screen.

A "pop-up" menu is similar, but appears automatically when certain choices are made. For example, if a user selects the "Parameter File" option from a pull-down menu, a pop-up menu appears under the first option, allowing to select a sub-menu choice. Once the choice is made, the pop-up menu disappears. Each menu appears in a "window", a separate area of the screen, surrounded by a border. These windows appear and disappear as needed. Each window supplies a list of options, which can be selected by moving up and down an highlight bar with the arrow-keys.

Thus, the ease of use of the program is mainly due to its menu with

windowed input screens where most of the time the arrow-keys or the Enter-key only are used to dialogue with the computer. Any input is automatically checked for proper form and length. The menu is a dBASE-III-PLUS work-alike. It is made up of a main menu bar containing six major modules: ALPHA, CALIBRATION, INTENSITY, SAMPLE, REPORT and UTILITIES. Each module provides several other options inside a pull-down window system. To dialogue with the computer is then like navigating through pop-up windows, which appear and disappear as fast as you can press the arrow-keys. Furthermore, each option provides context sensitive on-line HELP windows. To select an option, press the F1-key and a full screen of information on the option appears. Press the Esc-key and you are back to the initial screen. Each pop-up window has a different colour, which is not essential but makes the analyst's work easier.

SOME OTHER FEATURES OF THE PROGRAM

The program is used to determine the chemical composition of homogeneous samples analyzed by X-Ray Fluorescence Spectrometry. It uses the fundamental algorithm to convert measured intensities into concentrations and to correct for inter-element effects. It can be used to analyze any kind of samples with large or limited range of composition.

To carry out the various operations of the program, the user need not be familiar with the fundamental-parameters method or the formulas that are used; they are obtained automatically from data files as required. To run the program, the user should only supply the measured intensities from a few standard reference materials, their compositions, measured intensities of unknowns and concentrations of unmeasured components, if any.

The program provides a wide range of facilities, which allow you:

* To create, update or print a file of all fundamental parameters required to analyze a new series of analytes.

* To calculate and print any X-ray tube output spectrum using the accurate and efficient mathematical model proposed by Pella et al.[7].

* To Calculate and print the theoretical influence coefficients in the Claisse-Quintin (CQ) algorithm for any kind of systems. For the user, calculations are as easy as entering the name of the analyte. The program takes care of all complex aspects of the theory and automatically supplies all fundamental parameters: mass absorption coefficients, fluorescence yields, jump ratios, and line and edge wavelengths. Mass absorption coefficients are calculated from a judicious mix of the Heinrich[8] and of the Leroux & Thinh[9] data.

* To enter, correct or print the composition of calibration standards.

* To calculate Alpha and Rho coefficients in the fundamental algorithm for any standard. The theoretical relative intensity of each analyte is also calculated.

* To perform a unique calibration process with high-quality graphical output. It matches the theory with the reality by referring to standards. A few only, two or three, are required for the calibration of a given analyte and these do not have to be similar to the unknowns. The pure elements are not required.

* To determine a series of working conditions appropriated to your laboratory. For example the program asks you if you want to enter intensities by hand or from a file, to enter net or gross intensities, to enter sample names with the present program or not, etc.

* To transform measured intensity files into working files of net intensities in a format compatible with the program, after having subtracted the background, any blank and corrected for any interference on each measured peak. It is also possible to enter intensities by hand.

* To create a master file to store all the calculated concentrations of unknown samples, which can be read, printed, updated or deleted.

* To convert the measured net intensities into concentrations using the CQ algorithm to get a first estimate of the sample composition. Then, the final composition is calculated with the fundamental algorithm for up to 24 analytes. The program allows you to enter the concentrations of unmeasured components and to correct for them.

* To print final results in a report of analysis, in a format selected by the analyst, ready for distribution.

* To provide data transmission to or from an external computer.

* To use some utility options for access to the data files, to edit them or to execute other related duties.

In short, the program is a complete "off-line" package to perform XRF analysis. It is also universal, flexible, easy to use, accurate, applicable to specimens of any composition that are homogeneous with a flat and polished surface.

WORKING PHILOSOPHY

The basic philosophy of the program is to enter a minimum of information when you use it and every data entry must be saved for further use. The program also allows easy editing of all these data. The program must also supply all possible answers for any given question. To achieve all these goals the following approach is used.

When you execute an option, you dialogue with the system by answering to a series of questions. And no matter what the question, all the possible operator inputs are always shown between two square brackets ([ ]), followed by a colon, a default and then the symbol ' := ', after which the cursor stops and waits for your answer, as in the following example:

```
X-ray tube anode [ Sc, Cr, Mo, Rh, Ag, W, Au ] ...:      Rh :=
X-ray tube voltage [ 10 - 100 ] KV ..............:      40 := 60
Anode angle [ 10.0 - 90.0 ] Degrees .............:    18.0 :=
Thickness of Be window [ 0.125 - 0.500 ] Mm .....:   0.150 :=
Last wavelength of spectrum [ 2.5 - 8.0 ] A .....:    7.09 :=
Tube filter [ Y/N ] ? ...........................:      No :=
Write X-ray tube spectrum to disk [ Y/N ] ? .....:     Yes :=

Is there any error [ Y/N ] ? ....................:      No :=
```

You can accept the default simply by pressing the Enter-key or enter a new answer, which may be either numbers or strings of alphanumeric characters and then press the Enter-key. In the above example, only the voltage is updated from 40 to 60 KV. For all the other questions, the proposed default was accepted as a new answer. Most of the time, the defaults are the last series of data entered. For example, if you enter "YES" to the last question, the same series of questions will be displayed again and all defaults become the last data just entered. Note that after any series of questions, the above last question is always displayed, giving the operator the opportunity to correct any wrong answer.

CONCLUSION

A new program has been described for the analysis of any kind of material by XRF. By so doing, an example of a modern program is presented. It is not claimed that this program is neither the best nor the only solution to the XRF analysis problem. There may exist a more elegant solution. However, the producers of some commercial products would be wise to inspire themselves from this work in order to make their programs much more easy to use and accurate, in other words, to make a reality the idea "painless XRF analysis".

Today, quantitative methods are no longer a problem and now software of high-quality is available. The last step now depends on the user himself, it is up to him to use it or not, to make pressure on companies producing WDS spectrometers to supply better quantitative software products. In the end the technique must benefit from it by becoming really easy and enjoyable to use and accurate.

Any analyst who has any suggestions to improve the XRF programs in general, or requires additional information, or wishes to test the present program, should write to the author.

REFERENCES

1. R.M. Rousseau, Concepts of Influence Coefficients in XRF Analysis and Calibration, (Also published in the present book).
2. R.M. Rousseau, X-Ray Spectrometry, 13, 115, (1984).
3. R.M. Rousseau, X-Ray Spectrometry, 13, 121, (1984).
4. R.M. Rousseau and M. Bouchard, X-Ray Spectrometry, 15, 207, (1986).
5. R.M. Rousseau, X-Ray Spectrometry, 16, 103, (1987).
6. Datastorm Technologies, Inc., P.O. Box 1471, Columbia, MO 65205, U.S.A.
7. P.A. Pella, L.Y. Feng and J.A. Small, X-Ray Spectrometry, 14, 125, (1985).
8. K.F.J. Heinrich, The Electron Microprobe, p. 296. Wiley, New York (1966).
9. T.P. Thinh and J. Leroux, X-Ray Spectrometry, 8, 85, (1979).

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CONCEPTS OF INFLUENCE COEFFICIENTS IN XRF ANALYSIS AND CALIBRATION

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ABSTRACT

It will be shown that there are different types of influence coefficients to correct for matrix effects in XRF analysis: the empirical coefficients calculated from regression analysis and valid for the standards on hand only; the theoretical binary coefficients that are essentially constant in a given concentration range; then the theoretical multi-element coefficients calculated from one given composition and valid for one specimen only.

With theoretical coefficients, however, a special calibration process is needed, because theory cannot take into account all the instrumental parameters. In the proposed calibration method it will be shown that the slope of the calibration curves is the link to correlate the theoretical formalism to the experimental reality; that the standards used do not have to be similar to the unknowns and that a few only are required; that the calibration curves can be extrapolated by a factor of two or three; that pure analytes are not required.

INTRODUCTION

In X-Ray Fluorescence (XRF) analysis, the influence coefficient approach assumes that measured intensities can be corrected for matrix effects (absorption and enhancement) by means of numerical coefficients that depend on the matrix composition. These "multi-element coefficients" can be calculated from theory, using the Fundamental Parameters equations[1,2,3], or can be determined empirically by regression analysis[4]. While the empirical coefficients depend specifically on the composition of the standards used, a set of theoretical coefficients calculated from a specimen composition is "unique" because each specimen composition is "unique". Any other specimen containing the same elements but in different proportions, or any other set of standards, will generate different sets of influence coefficients.

This last property of influence coefficients has caused problems to the XRF analysts and is the reason why approximate methods have proliferated[2,4,5,6] between the years 1960 and 1980. Those methods were based on the hypo-

thesis that the total matrix effect on the analyte i is equal to the sum of the effects of each element j of the matrix, calculated independently of each other. With these methods it was then possible to calculate a set of "binary coefficients" valid for a given composition range rather than for a given specimen. In other words, with binary coefficients it is assumed that the coefficient a_{ij} is a CONSTANT for a given range of C_i and C_j rather than being a VARIABLE dependant on the whole matrix composition. It will be shown that some of these methods are still valid as long as they are used with theoretical binary coefficients[5,7,8].

At the beginning of the 80's, new powerful quantitative methods, based on the "Fundamental-Parameters" approach and/or on the new concepts of theoretical coefficients, have been proposed mainly by J.W. Criss[5], R.M. Rousseau[3,10] and N. Broll[11]. The last two papers propose methods for calculating theoretical influence coefficients as a function of the composition of the matrix. These coefficients are called "multi-element coefficients" because they depend on the full composition of the matrix. For each specimen, an estimate of the matrix composition must be calculated first in order to calculate the multi-element coefficients and finally to calculate from them a more accurate composition of the specimen. This approach will be discussed in the present paper.

The two types of theoretical influence coefficients, binary and multi-element, are powerful tools to correct for matrix effects as long as a link exists for adapting the theory to the experimental reality, considering that no theory accounts for all experimental variables. It will be shown that an appropriate calibration process corrects for the imperfections of the theory and has a few other major qualities that facilitate the work of the analyst.

BINARY COEFFICIENTS

Lachance and Traill[5] were among the first to propose influence coefficients as a method of correction for matrix effects in XRF analysis. One of the most important ideas proposed in their paper is that the so-called "Alpha coefficients", can be calculated from theory. The proposed theoretical expression to calculate these is

$$\alpha_{ij} = \frac{\overset{*}{\mu_j}}{\overset{*}{\mu_i}} - 1 \qquad (1)$$

where $$\overset{*}{\mu_j} = \mu_j(\lambda_k) \operatorname{cosec} \phi' + \mu_j(\lambda_i) \operatorname{cosec} \phi'' \qquad (2)$$

$\mu_j(\lambda_k)$: mass absorption coefficient of j for the wavelength λ_k of the incident spectrum
$\mu_i(\lambda_i)$: mass absorption coefficient of j for the characteristic wavelength λ_i of i
ϕ', ϕ'' : incidence and take-off angles of X-ray beam

Equation (1) is an excellent start but it is valid for one given wavelength (λ_k) only of the incident spectrum. It also assumes incorrectly that enhancement behaves as a negative absorption and that α_{ij} is independent of the elements other than i and j.

To overcome these limitations, many approximate methods to correct for the matrix effects and to convert measured intensities (I_i) into concentrations (C_i) have been proposed. Among the proposed algorithms, three are more generally favoured for their accuracy and their solid theoretical foundation. They also use the modern concepts of theoretical binary coefficients. They are:

First, the Lachance-Traill algorithm[5]

$$C_i = R_i \{ 1 + \Sigma_j a_{ij} C_j \} \quad (3)$$

where R_i is the ratio of the measured net intensity I_i to the measured net intensity of the pure analyte i. The binary coefficient a_{ij} is calculated using equation (16) of reference (3) for the special case of a binary standard having a composition (C_{i*}, C_{j*}), where C_{i*} is the mid-value of the calibration range of the analyte i and where

$$C_{j*} = 1 - C_{i*} \quad (4)$$

This approach assumes that the coefficient a_{ij} is a CONSTANT (it is an approximation!) when applied to samples with a limited concentration range (0-10%), for example, oxides in rock samples in fused disks. A theoretical mean relative error of 0.02% on the calculated concentrations[12] is expected.

Secondly, the Claisse-Quintin (CQ) algorithm[7]

$$C_i = R_i [1 + \Sigma_j (a_{ij} + a_{ijj} Q_M) C_j + \Sigma_j \Sigma_k a_{ijk} C_j C_k] \quad (5)$$

where the matrix concentration

$$Q_M = C_j + C_k + \ldots \quad (6)$$

and where the "crossed" coefficients a_{ijk} are included to compensate for the fact that the total interelement correction cannot be strictly represented by a sum of binary matrix effects. The coefficients are calculated by equations (4,5,6) of reference (10). Contrary to Wadleigh's claim[13], the latter equations do not contain errors when they are compared to those of Rousseau and Claisse[14], they are only improved and more accurate.

The influence coefficients of the CQ algorithm are considered as constant when applied to samples with a medium concentration range (0-40%), for example, oxides in cement samples in pressed pellets. In this case, the method introduces a theoretical mean relative error of 0.04% on the calculated concentrations[12].

Thirdly, the Lachance algorithm[8]

$$C_i = R_i \{ 1 + \Sigma_j [a_1 + \frac{a_2 Q_M}{1 + a_3 (1 - Q_M)}] C_j + \Sigma_j \Sigma_k a_{ijk} C_j C_k \} \quad (7)$$

where the binary coefficients a_1, a_2, and a_3 are calculated by means of equations (A6) of reference (8) and the crossed coefficients a_{ijk} by the equation (19). This algorithm can be applied to samples with a large concentration range (0-100%), for example, elements in alloys. In this case, the method introduces a theoretical mean relative error of 0.3% in the calculated concentrations[12].

An experimental verification of these three algorithms done by Pella et al.[15], confirms the expected theoretical accuracy. Consequently, the XRF analyst should consider the theoretical binary coefficient approach within these three algorithms as a good alternative to the fundamental parameters approach, specially when the matrix effects or the variations in composition are small.

However, the calculation of theoretical coefficients cannot be done without computer programs. The public domain program, NBSGSC[16], performs all the XRF analysis calculations on a DIGITAL PDP-11 minicomputer. The commercial version of this program[17] and a few others such as CiLT, CiLAC and CiROU[18], running on an IBM-PC, are also available.

EMPIRICAL COEFFICIENTS

Coefficients for matrix effect corrections can be obtained by multiple regression methods using measured intensities and standard compositions, which cover the analyte concentration ranges of interest. These correction coefficients are called empirical coefficients. The Rasberry and Heinrich model[4] is a good example of this approach. The success of empirical coefficients depends on the availability of standards that closely match the compositions of the unknowns. As the number of analytes increases, so does the number of standards required.

The preparation and measurement of an adequate number of reliable standards could be long and tedious and can easily yield empirical coefficients that are often not accurate and have no physical meaning. This statistical approach is sensitive to any error in the data and the calculated coefficients can be applied ONLY to unknowns of composition similar to those of the standards used.

An easier and much more practical solution to these problems is to compute theoretical coefficients. They can be calculated for any combination of elements and any experimental conditions, within of a few seconds! Use of empirical coefficients should then be discontinued to avoid potential problems and to minimize inaccurate results.

MULTI-ELEMENT COEFFICIENTS

A better approach than the empirical coefficients is the fundamental parameters method first proposed by Criss and Birks[2]. This method has been optimised by Criss[9] and can be applied through the computer program XRF-11 also developed by him. More details on the method and on the program performance are given in reference (19).

Alternately, new powerful quantitative methods, based on the fundamental parameters approach and on the new concepts of theoretical multi-element coefficients, have been proposed[3,10,20]. In particular, Rousseau[3], using the Sherman's equations[1], deduced new theoretical expressions for multi-element influence coefficients in which the correction for both absorption and enhancement effects are clearly and accurately defined. They are used in the fundamental algorithm

$$C_i = R_i \frac{1 + \Sigma_j \alpha_{ij} C_j}{1 + \Sigma_j \rho_{ij} C_j} \qquad (8)$$

where α_{ij} and β_{ij} are the multi-element coefficients correcting for absorption and enhancement, respectively. These are calculated by means of equations (9) and (10) in reference (3). The fundamental algorithm can be applied to any type of samples with any composition. The method introduces a theoretical mean relative error of 0.07% only[12].

An experimental verification of this method done by Rousseau and Bouchard[21] on different types of alloys confirms the accuracy and versatility of the method. To test this method the computer program CIROU V3.0 was developed by the Geological Survey of Canada and is in the public domain. It runs on DIGITAL PDP-11 minicomputers under the RSX-11M operating system. A more user-friendly version of this program is available from Corporation Scientifique Claisse[18]. It runs on IBM-PC/XT/AT, PS/2 or compatible computers under the PC/MS-DOS operating system.

CALIBRATION

Although in many cases the analysis of samples with limited composition range may allow the use of linear calibration curves (Intensity versus Concentration), it is usually more desirable to work with a general purpose calibration process which is applicable to a larger variety of matrix types over wider concentration ranges.

With theoretical coefficients, however, a special calibration process should be used, because it is well known that theory cannot account for all the instrumental parameters. The proposed calibration process is the following:

The relative intensity R_i is defined as the ratio of the net intensity of the analyte i to the net intensity $I_{(i)}$ of the pure analyte i :

$$R_i = \frac{I_i}{I_{(i)}} \qquad (9)$$

This equation can be written in the form of a straight line equation,

$$\frac{I_i}{I_{is}} = \frac{I_{(i)}}{I_{is}} R_i \qquad (10)$$

where both side of the equation have been divided by I_{is}, the net intensity of the analyte i in any monitor. The relative intensity can be calculated by the expression

$$R_i = \frac{C_i}{[\ 1 + \ldots\ ]} \qquad (11)$$

from any of the inverted algorithm (3), (5), (7) or (8) chosen by the analyst. The R_i intensities are calculated for all the standards on hand and their I_i and I_{is} intensities are measured. Then, if the MEASURED relative intensities I_i/I_{is} (Y-axis) are plotted as a function of the CALCULATED relative intensities R_i (X-axis), it gives a straight line of slope equal to $I_{(i)}/I_{is}$[10,21].

This calibration approach has the following clear advantages:

1. Since the curves compare two similar objects, calculated and measured relative intensities, they are independent of the composition of the standards used. Consequently, the standards do not have to be similar to the unknowns and such curves become universal calibration curves.

2. The calibration slope adjusts the theory to the experimental reality. If the pure analyte is used as monitor, the slope value is close to 1.0 but not necessarily equals to 1.0. The deviation from 1.0 come from the imperfection of the theory and the observed slope is the factor required to correct for that.

3. Pure analytes are not required, but their intensities are directly calculated from the slope of the calibration curves. If a few are available, they are handled as any other standard.

4. If a single point is off the calibration curve by more than the expected error, it clearly stands out and facilitates tracing eventual errors. In other words, the method is a "fail-safe" process.

5. Each analyte of a specimen can be calibrated independently of all other analytes. In this manner, if the calibration of one analyte has to be done again, this does not affect the calibration of the other analytes. Furthermore, the standards do not need to contain all the analytes of the specimen. Each calibration curve can be drawn from as few as one standard, which for example can be the pure analyte.

6. The calibration curves can be extrapolated by a factor of two or three, thus protecting the analyst from errors when the sample concentrations exceed the calibration range.

APPLICATION TO ANALYSIS

Once the slope m_i of the calibration curve of the analyte i is determined, the concentrations C_i of the unknowns are calculated from a combination of equations (10) and (11)

$$C_i = \frac{1}{m_i} \frac{I_i}{I_{i\,a}} [\ 1 + \ldots\ ] \qquad (12)$$

where the term in brackets is the matrix effect correction in the algorithm selected by the analyst.

CONCLUSION

Since there is no longer any need for empirical coefficients, only two types of influence coefficients remain. Firstly the theoretical binary coefficients that are constant in a given concentration range of C_i and are independent of the matrix composition. They are used in theoretically valid algorithms, such as the Lachance-Traill, Claisse-Quintin and Lachance algorithms. Secondly, the theoretical multi-element coefficients calculated from an estimate of the composition of each sample are then used in the fundamental algorithm to obtain a more accurate composition of the sample.

It is expected that the present explanations will eliminate the pseudo-ambiguities or pseudo-errors raised by some authors[13,22,23].

Without computer programs, theoretical coefficients can not be calculated. Some are already available but higher quality ones will be written in the future, making empirical and approximate methods less and less popular, specially when microcomputers become still more effective and less costly.

The proposed calibration process offers many advantages compared to the traditional calibration of intensities versus concentrations; it increases the accuracy of XRF analysis and facilitates the work of the analyst.

REFERENCES

1. J. Sherman, Spectrochim. Acta 7, 283, (1955).
2. J.W. Criss and L.S. Birks, Anal. Chem., 40, 1080, (1968).
3. R.M. Rousseau, X-Ray Spectrometry, 13, 115, (1984).
4. S.D. Rasberry and K.F.J. Heinrich, Anal. Chem., 46, 81, (1974).
5. G.R. Lachance and R.J. Traill, Can. Spectrosc., 11, 43, (1966).
6. R. Jenkins, Advances in X-Ray Analysis, 22, 281, (1979).
7. F. Claisse and M. Quintin, Can. Spectrosc., 12, 129, (1967).
8. R.M. Rousseau, X-Ray Spectrometry, 16, 103, (1987).
9. J.W. Criss, Advances in X-Ray Analysis, 23, 93, (1980).
10. R.M. Rousseau, X-Ray Spectrometry, 13, 121, (1984).
11. N. Broll, X-Ray Spectrometry, 15, 271, (1986).
12. R.M. Rousseau, G.S.C. Internal Report, October 1981.
13. K.R. Wadleigh, X-Ray Spectrometry, 16, 41, (1987).
14. R. Rousseau and F. Claisse, X-Ray Spectrometry, 3, 31, (1974).
15. P.A. Pella, G.Y. Tao and G. Lachance, X-Ray Spectrometry, 15, 251, (1986).
16. G.Y. Tao, P.A. Pella and R.M. Rousseau, NBSGSC - A FORTRAN Program for Quantitative X-Ray Spectrometric Analysis. NBS Technical Note 1213, National Bureau of Standards, Washington, DC (1985).
17. RAINIER SOFTWARE, 2414 S.E. Mud Mt. Rd., Enumclaw, WA 98022.
18. CORPORATION SCIENTIFIQUE CLAISSE INC., 2522 chemin Sainte-Foy, Sainte-Foy, Quebec, Canada, G1V 1T5.
19. D.B. Bilbrey, G.R. Bogart, D.E. Leyden and A.R. Harding, X-Ray Spectrometry, 17, 63, (1988).
20. N. Broll and R. Tertian, X-Ray Spectrometry, 12, 30, (1983).
21. R.M. Rousseau and M. Bouchard, X-Ray Spectrometry, 15, 207, (1986).
22. R. Tertian, X-Ray Spectrometry, 15, 177, (1986).
23. G.R. Lachance, Advances in X-Ray Analysis, 31, 471, (1988).

ANNEXE - C

PROPOSITIONS DE RECHERCHE DES LSM
(LLOYD DALTON)

Government of Canada / Gouvernement du Canada

MEMORANDUM NOTE DE SERVICE

To / A: A. Boyer
MRL

From / De: J. L. Dalton
MSL - Chemical Laboratory

Security Classification – Classification de sécurité	
Our File – Notre référence	
Your File – Votre référence	
Date	11 January 1990

Subject / Objet: MSL Proposal for Gold measurement in ores; Results of Meeting on January 4, 1990

Introduction

It would be highly desirable to have available a rapid method of measuring gold concentration, at the ore grade level, right at the drill site. However considering the low level of the ore grade, say 10 ppm, the demands upon the instrumentation are considerable. As far as is known, there is at present no proven instrumentation or methodology to accomplish this measurement. X-Ray Fluorescence instrumentation has been developed to measure gold at ore grade concentration by a British firm for the South African gold fields, in the laboratory mill at a mine site. The measurement is accomplished using the K lines of gold with complex automated instrumentation costing approximately $500,000. An American firm tried to develop portable XRF instrumentation to work at a mine face but it failed to produce satisfactory results after some ten years of continual testing and modification. The work was carried out at the Giant Yellowknife mine.

A meeting was held January 4, 1990 between MSL and MRL staff to seek solutions to this problem. After some discussion, it was decided that the two most promising approaches would be X-Ray Fluorescence using K-lines and a rapid wet-chemical geochemical-type test.

Given the expertise available in MSL, it was suggested that MSL prepare a proposal to evaluate these two approaches.

Canada

X-Ray Fluorescence (XRF)

MSL has awarded a contract to U. of Western Ontario to do laboratory measurements using the K lines of Au, using the radioisotope Ba-133. The purpose of this contract is to demonstrate the feasibility of using this radioisotope. (The results of the feasibility test should be known by the end of March, 1990). If successful at the 20 ppm level with a ten minute measurement, then efforts will be made to design an instrument suitable for use in a mill environment at the mine site for measurements, at the ore concentration level. The design efforts will be strongly focused on the sample-radioisotope-detector geometry. The X-ray detector and electronic processing instrumentation that will be used in a prototype will be commercially - available modules.

An American firm, SCITEC CORPORATION, has developed a portable XRF instrument to measure gold using the K lines with Co-57 as the radioactive isotope. This radioisotope is quite capable of exciting the K lines of gold, but the lowest concentration that can be determined remains unknown. Only thorough testing on representative samples can be used as an indicator, but as a first step, MSL should send its gold reference materials to the firm for analysis.

At the meeting, it was mentioned that MRL is prepared to rent an instrument from SCITEC for evaluation purposes. MSL is prepared to cooperate in the evaluation of the instrument, but arrangements would have to be made for representative sample availability.

2. Rapid Wet-Chemical Testing

It is known that there are many field methods available for rapid testing to confirm presence or absence of a particular element. To apply this concept, chip samples would have to be crushed and ground, acid-digestion followed by reagent addition for some type of visual estimation. It is estimated that this type of operation could be carried out in a mill environment, and possibly in the mine, with a target turnaround time of a few hours per batch.

The plan for this approach would be a literature search and evaluation, test method selections, preparation of cost estimates and finally preparation of work plan. There would have to be a developmental/research component to the plan to ensure that a proposed test method is capable of producing the measurements.

Very likely, this would involve the use of contract funds. For instance, is it possible to develop test-paper for gold measurement in the same way that clinical tests are carried out for ketones and sugars in urine?

3. Cost Considerations

Since MSL is already involved in the XRF aspect of gold measurement, the cost considerations, in terms of a PY charge to an MRL project, are minimal. However, the other approach would require the services of a professional chemist, at the CH-2 or RES level for at least 0.15 PY to develop a work plan and 0.25 PY to investigate and evaluate reagent test methodology. Also, there may be a requirement for contract funds to develop a test reagent or possible test paper.

J. T. Dalton

Government of Canada / Gouvernement du Canada

MEMORANDUM **NOTE DE SERVICE**

To / A: Andre Boyer
MRL

From / De: Lloyd Dalton
MSL

Security Classification – Classification de sécurité
Our File – Notre référence
Your File – Votre référence
Date: 12 December 1989

Subject / Objet: **Re: Further to your inquiry concerning Au determination for exploration and process control purposes, I have prepared the following brief background**

Solids

Enclosed is a copy of the work statement to examine the possibility of using a relatively inexpensive system to measure gold in solids by X-ray fluorescence analysis. It will be a few months before a detection limit can be established, which will decide its practicality.

I believe I mentioned that I sent reference materials overseas for analysis by the British commercial instrument. Their analysis was very good, within the estimated error for the two materials. But the cost of this instrumentation is very high, some $600,000.

I have always wondered why the concept of bore-hole logging could not be used in mining practice. Pat Killeen of the GSC has demonstrated that this technique can be very accurate for base metals. I don't know whether he has looked at Au or not.

Solutions

(i) Atomic-Absorption Spectrometry

An on-line automated system appears to be feasible. Laboratory measurements obtain a detection limit of 0.1 ppm, which should be suitable. As laboratory-type automatic sample feeding is available, it would appear that sampling and pumping stations could be designed to bring a solution from a point in the mill to a centrally-located spectrometer, as is done with X-ray fluorescence on-line instrumentation.

(i) Fluorescence Spectrometry

Exploratory work has been done by York University and Scintrex. This work was funded by NRC PRAI grant programs. I was the Scientific Authority. The objective of this exercise was to expand the capabilities of the laser instrumentation developed by Scintrex for uranium determination. Dr. A.B.P. Lever's work at York University showed that an Au determination could be carried out with laboratory-type fluorescence instrumentation. However, I do not believe that definitive work was ever carried out.

Further research work would have to address the matrix effect of mine/mill solutions, including an extraction of the Au into an organic solvent, adapting the existing Scintrex laser system to a gold measurement and finally adapting the laboratory instrument to an industrial configuration. Although this may appear very complex, it should be noted that Rio Algom at Elliot Lake are using a Scintrex laser system for process control measurements.

There is some indication that the fluorescence measurement system could be integrated into a separation-measurement system employing state-of-the-art techniques. High Pressure Liquid Chromatography could be used for the separation aspect and fluorescence spectroscopy for measurement. Ideally, the fluorescence spectra would be an instrument similar to the Scintrex uranium determination instrumentation.

Lloyd Dalton

Lloyd Dalton

c.c. R. McDonald
H.F. Steger
D.J. Barkley

Supply and Services Canada / Approvisionnements et Services Canada

Supply and Services Canada
Science Branch
11C1 Phase III
Place du Portage
Hull, Quebec K1A 0S5

REQUEST FOR PROPOSAL
DEMANDE DE PROPOSITION

Date of Solicitation - Date de l'invitation
06 Oct/oct 1989

Address enquiries to: - Adresser toute demande de renseignements à:
P. Hurtubise

Area code / code régional	Telephone No. / N° de téléphone	Extension / Poste	Telex No. / N° de télex
819	956-1360	0	053-3703

Destination
DEPT. ENERGY, MINES & RESOURCES
OTTAWA, ONTARIO, K1A 0G1

Proposal to: Supply and Services Canada

We hereby offer to sell to Her Majesty the Queen in right of Canada, in accordance with the terms and conditions set out herein, referred to herein or attached hereto, the services listed herein and on any attached sheets at the price(s) set out therefor.

Proposition aux: Approvisionnements et Services Canada

Nous offrons par la présente de vendre à Sa Majesté la Reine du chef du Canada, aux conditions énoncées ou incluses par référence dans la présente et aux annexes ci-jointes, les services énumérés ici et sur toute feuille ci-annexée, au(x) prix indiqué(s).

Instructions: (Additional instructions appear on reverse side).

Municipal taxes are not applicable, for provincial taxes, see reverse.

Unless otherwise specified herein by the Crown, all prices quoted are to be net prices in Canadian funds including Canadian customs duties, excise taxes, federal sales tax and are to be F.O.B. including all delivery charges to the destination(s) as indicated.

Instructions: (On trouvera de plus amples instructions au verso).

Les taxes municipales ne s'appliquent pas, voir au verso pour les taxes provinciales.

Sauf indication contraire, énoncés par la Couronne, dans les présentes, tous les prix indiqués sont des prix nets, en dollars canadiens, comprenant les droits de douane canadiens, la taxe d'accise, la taxe fédérale de vente et doivent être F.A.B., y compris tous frais de livraison à la (aux) destination(s) indiquée(s).

Country of Foreign Content / Pays d'origine des éléments étrangers	Value of Foreign Content / Valeur des éléments étrangers
U.S.A.	$ 4,450. CDN

Delivery required - Livraison exigée	Delivery offered - Livraison proposée
31 Mar/mar 1990	31 March 1990

Solicitation closes - L'invitation prend fin	SSC file No. - N° de référence d'ASC
at-à 1400 EDT / HAE on-le 25 October 1989	028SQ.23440-9-9112/S

Please ensure this area appears in window of return envelope
S'assurer que cette partie figure dans la fenêtre de l'enveloppe-réponse

Vendor Name and Address - Raison sociale et adresse du fournisseur

The University of Western Ontario
London, Ontario, Canada
N6A 5B9

Telephone No. - N° de téléphone (519) 661-3393

Name and title of person authorized to sign on behalf of vendor (type or print)
Nom et titre de la personne autorisée à signer au nom du fournisseur (caractère d'impression)

SUSAN HODDINOTT
ASSISTANT DIRECTOR
RESEARCH SERVICES

Signature Susan Hoddinott Date 25 Oct. 89

Canada

DSS-MAS 9400-2 (07/88)

OBJECTIVE

To evaluate the determination of gold in ores and mill products using the radioisotope Ba-133 as an excitation source and the measurement of the Au K lines.

BACKGROUND

The purpose of this investigation is to seek a private sector partner to investigate the determination of Au in massive powdered samples via K line measurement. It is estimated that the infinite thickness for the Au K_α X-ray is of the order of 3 cm and therefore large volume sampling with X-ray fluorescence becomes a possibility.

Commercial instrumentation is available which utilizes the K X-rays of Au, but excitation is accomplished with an X-ray tube and generator. The detection limit is less than 1 ppm, but the cost of this complex instrument is over $500,000. We propose a simpler, less expensive instrument by using radioisotope excitation.

The isotope Ba-133 emits a gamma-ray at 80.998 KeV, with a relative probability of 0.52. The Au K absorption edge is at 80.713 KeV. The proximity of the gamma-ray to the absorption edge shows highly effective excitation. The half-life of Ba-133 is 10.9 years. Furthermore, the gamma-ray at 80.998 KeV will not excite the K lines of lead and therefore lead can be used as shielding material without experiencing spectral interference on the Au K_α line.

It has been reported that Cd-109 can be used as effective excitation for Au (1), but the half-life of Cd-109 is 453 days, considerably shorter than Ba-133 and the Cd-109 gamma-ray is very effective in exciting lead.

CONTRACTOR REQUIREMENTS

The contractor's laboratory will have to be equipped with radiation measurement instrumentation including a high-resolution, liquid nitrogen-cooled gamma-ray detector, suitable for use in the energy range of 60-90 KeV. The contractor will need a license from the Atomic Energy Control Board for the use of ~4 gigabecquerels of Ba-133. CANMET may give consideration to potential contractors who propose undertaking this study using CANMET facilities. In such an instance, a charge for facility usage will apply and be considered to be part of the CANMET $25,000 contribution to the contract.

The design of the assembly incorporating the excitation source(s) and sample arrangement around the gamma-ray detector will be the joint responsibility of the contractor and the Scientific Authority. The design of such assemblies is covered in some detail in references 2, 3 and 4. While the use of annular sources offer simplicity of design and construction, utilization of several capsule sources offer optimization of excitation, as detailed in reference 4 which is favoured by the Scientific Authority. The construction of the assembly and making the radiation measurements will be the responsibility of the contractor. Materials for analysis will be supplied by the Scientific Authority.

The contractor will be expected to supply personnel with several years of experience in radiation measurement and at least familiarity with design of radioisotope assemblies for energy-dispersive X-ray fluorescence analysis.

The six phases of the project are as follows:

1. Obtain approval from the Atomic Energy Control Board and order 3.7 gigabecquerels of Ba-133 from a suitable supplier.

2. In conjunction with the Scientific Authority, design a suitable sample-excitation housing assembly.

3. Construction of the sample-excitation housing assembly at the contractor's laboratory.

4. Sample measurement on material supplied by the Scientific Authority.

5. Data analysis and evaluation.

6. Report preparation.

The Ba-133 source remains the property of the Crown and will be returned to it at the completion of the contract.

COST ESTIMATE

It is expected that the cost of the project will be $35,000-$40,000. CANMET will provide $25,000. Consideration will be given only to potential contractors who are prepared to share in the cost of this contract at an effort of approximately $10,000 minimum.

ANNEXE - D

INFORMATION TECHNIQUE SUR LE RADIOMÈTRE (HHRR) DE BARRINGER RESEARCH LTD.

613-995-3456

BARRINGER

304 Carlingview Drive
Metropolitan Toronto
Rexdale, Ontario, M9W 5G2
Phone: 416-675-3870
Telex: 06-989183
Fax: 416-675-3876

FACSIMILE COVER SHEET / MESSAGE FORM

To: Mineral Research Labs, CANMET

Attention: M. André Boyer

From: Canum Cumming

Date: Jan 3/90

Total number of pages (including this one): 3

Data on the core viewing
attachment re HHRR.
Literature also is in the mail
Bonne chance.

If you do not receive all pages, or any parts of the transmission are illegible, please telephone (416) 675-3870 immediately.

BARRINGER RESEARCH

BARRINGER RESEARCH LIMITED
304 CARLINGVIEW DRIVE
METROPOLITAN TORONTO
REXDALE ONTARIO
CANADA M9W 5G2
PHONE 416-675 3670
TELEX 06-989185

ACCESSORY

HAND HELD RATIOING RADIOMETER

HHRR CORE VIEWING ATTACHMENT (CVA)

1. REQUIREMENT

The conventional HHRR can be used to view targets at distances from 1.2 m (4 ft.) to infinity. Since the field of view of HHRR is 2 deg. x 12 deg., the minimum size target at 1.2 m is 43 x 250 mm (1.7 x 10 inches). Since drill cores are of smaller diameter, the CVA was constructed to allow for a minimum target size of 11 x 65 mm (0.4 x 2.55 in.) at a nominal distance of 254 mm (12 in.).

2. CONSTRUCTION

The CVA acts somewhat as a close-up lens in front of a camera, and somewhat as if two small prisms were placed over the two optical channels of HHRR. Its housing is of molded plastic in which are mounted rigidly two sectors of an infrared transmitting quartz lens of focal length 305 mm (12 inches) at 500 nm.

3. INSTALLATION

Turn out the two mounting screws at the ends of the CVA. Place the CVA over the front end of the HHRR. Secure the CVA by tightening the two screws. Set FOCUS to (infinity).

The alignment of HHRR to look at a near-minimum size target should be done with care. Place drill core or other small line target in front of HHRR silhouetted against blackness. Select filters such that both CH1 and CH2 have useful signals. Align target and radiometer viewing direction so that CH1 and CH2 signals are full valued, with insensitivity to slight changes in alignment. Operate HHRR as described in the manual. With CVA attachment, take special precautions to avoid shadows and nearby "coloured" objects. See Section 3, paragraph i9

4. TARGET DISTANCE

The focal length of the lens segments in the core attachment changes with wavelength. Although the correction is small, it is recommended that the following table be used in selecting the appropriate target distance.

BARRINGER

304 CARLINGVIEW DRIVE
METROPOLITAN TORONTO
REXDALE, ONTARIO
CANADA M9W 5G2
PHONE: 416-675-3870
TELEX: 06-989183

November 2, 1989

Mr. Andre Boyer
CANMET
Energy Mines and Resources Canada
555 Booth Street
Ottawa, Ontario
K1A 0G1

Dear Mr. Boyer:

Further to our recent telephone conversation, I am pleased to send you some reprints and brochures describing our Hand Held Ratioing Radiometer (HHRR) and some preliminary studies on the correlations between HHRR reflectance ratios, geochemistry and XRD analysis of hand samples and drill cores from several gold deposits.

The current status of this method may, I think, be fairly described by saying that the basic hardware is well developed and proven in field use, but more development is needed to refine the algorithms, to establish the accuracy by extensive field testing and to engineer the system for automated operation by non-specialist personnel.

I hope you will find this helpful; if you have any further questions, please let me know.

Yours very truly,

BARRINGER RESEARCH LIMITED

Robert Dick

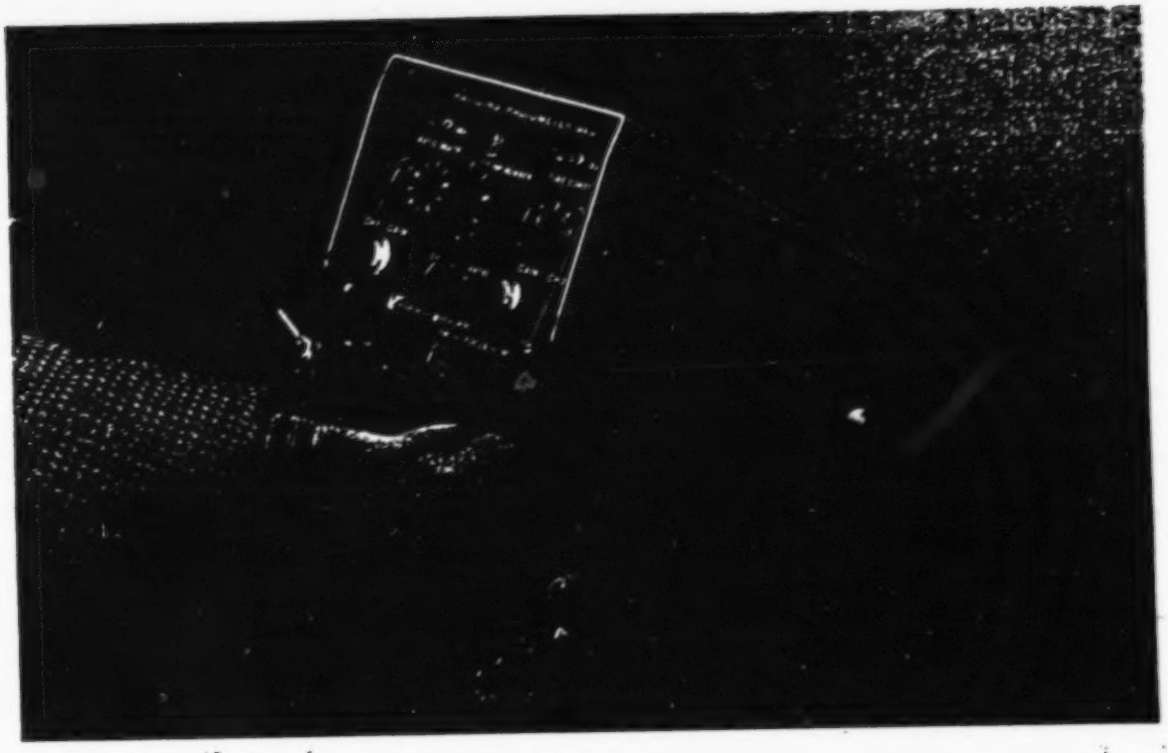
R. Dick

RD:aw
Encl: AIME paper
Application of Reflectance Spectrometry to Mineral Exploration Using Portable Radiometers
HHRR Brochure
HHRR Application Release #1
Microflex Brochure
Geneq Brochure

BARRINGER RESEARCH

RATIOING RADIOMETER* MK II

Hand Held Reflectance Radiometer (HHRR) for the Earth Sciences



DESCRIPTION

The instrument is a self-contained, dual beam ratioing radiometer with two optical trains directed at the same target. It provides a continuous digital readout of the radiance from the two optical trains. Each optical train has a separate 5 position filter wheel for selection of spectral bands. Each individual channel signal or the ratio of the two channels can be displayed for identification of a particular target, on the basis of known spectral characteristics of the target.

Positive target identification can be achieved by measuring the ratio of the two most prominent spectral peaks characterizing the target. The instrument can provide a selective ratio of such spectral peaks in any of up to 25 pairs of pre-selected narrow bands in the spectral range from 0.4 micrometres to 2.8 micrometres.

The radiometer is simple to operate and requires minimal skill. Field calibration is carried out using a standard reflectance reference having a high reflectance throughout the spectrum. The HHRR can be used with solar radiation or with a quartz-halogen lamp.

The portable radiometer system comprises the Ratioing Radiometer, a Battery Pack, and Standard Reflectance Target Package that are belt mounted, a shoulder strap, and a carrying/shipping case. Sets of Narrow Band Filters are available to suit a wide variety of applications, including the LANDSAT and SPOT satellite bands.

**Developed by California Institute of Technology at Jet Propulsion Laboratory during research sponsored by NASA. Manufactured and sold by Barringer under exclusive license from California Institute Research Foundation.*

TYPICAL APPLICATIONS:

General Studies	Water quality; soil moisture content; ground truthing for remotely sensed data, (covers NASA Thematic Mapper and LANDSAT bands):
Agriculture	Crop health and vigour; maturity and stress; agricultural land use; grazing lands analysis; pollution effects on forest cover; forest speciation;
Geobotany	Spectral reflectance changes caused by mineralization induced stress
Geochemistry	Detection of geochemical alteration haloes
Geology	Outcrop detection and geological mapping; soil, overburden and rock classification; stratigraphical studies; examination of lithological facies changes
Exploration	Hydrothermal alteration patterns; diamond drill core and oil well drill cutting logging
Oceanography	Coastal and estuarine studies; water colour; algae growths; shoaling; limnological studies and turbidity; hydrology stress
Geo Technology	Soil mechanics; earth stability studies; engineering geology; clay content of ores.

Barringer staff will be pleased to discuss other applications, and have a large library of spectral signatures to call upon.

A scanning field reflectance spectrometer covering the same working spectral range of this instrument, 0.4 to 2.5 microns, is available to enable correct selection of filters for various user applications.

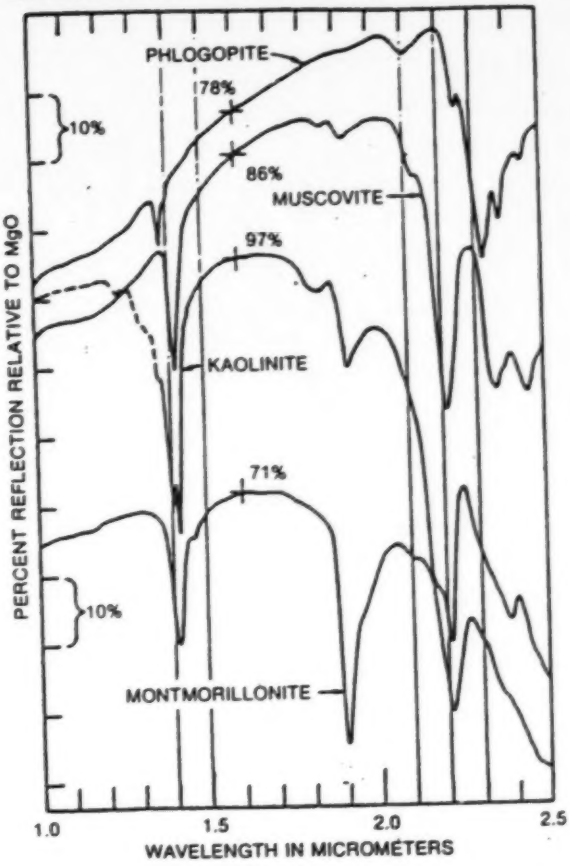
DESIGN FEATURES:

- Chopper provides AC signal to the two detector channels.
- Two balanced detectors simultaneously measure radiance through filters.
- Signal obtained by ratioing the detector outputs after amplification and rectification.
- Continuous digital readout of radiometric signal on a liquid crystal display. Analog output available for recording.
- Readout of either channel separately or ratio signal, switch selectable.
- External reflectance reference target verifies balance and calibration of the instrument.
- Common field of view (FOV) for both channels, 4 feet to infinity (parallax compensation).
- Light weight, hand held, battery operated, truly portable. Rugged construction for field service.
- Liquid crystal display of radiometric ratio, single channel radiance, detector temperature and battery state via switch selection.
- LCD indicator of chopper out of lock; detector cooler failure.
- Both sections of the filter wheel accommodate 5 filters each in mounts for easy exchange.

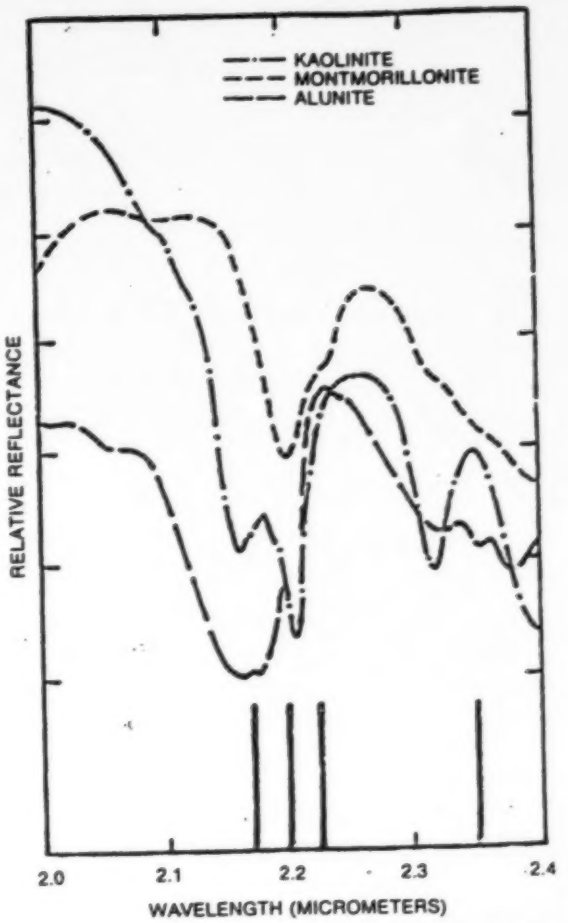
OPERATIONAL FEATURES:

- Ratio operation compensates for illumination changes.
- Calibration against standard reference target compensates for solar/sky spectral changes.
- Solar radiation or artificial source may be used.
- Insensitive to thermal drifts and gradients within the unit.
- Wide selection of filters available for different applications.
- Simple to use, calibrate and interpret.
- Filter positions in either channel easily switch selectable to move independently or as preset matched pairs.

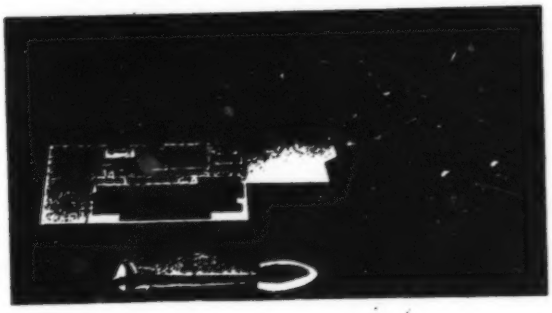
SPECTRA OF ALTERED ROCKS



Features due to vibrational processes in the spectra of four hydroxyl-bearing minerals commonly present in hydrothermally altered rocks. Spectra are displaced vertically. Reflection values are indicated on the curves at 1.6 μ m.



Laboratory spectra of selected minerals (layer silicate) from Hunt (USGS). The bars on the ordinate indicate location of centres of four of the radiometer channels.



Optional accessories: Data logger, Light source, Tripod, Integrating Sphere, FOV Twist Attachment.

Through the selection of the two filters for ratioing, a wide range of applications can be addressed. Thus the two filters can be closely set together for detecting very subtle fine structures, as in clay minerals, as illustrated to the left.

Alternatively the filters can be spaced far apart. Filter position selection depends upon the application.

For further information contact:

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Telex: 06-989183
Fax: 416-675-3876

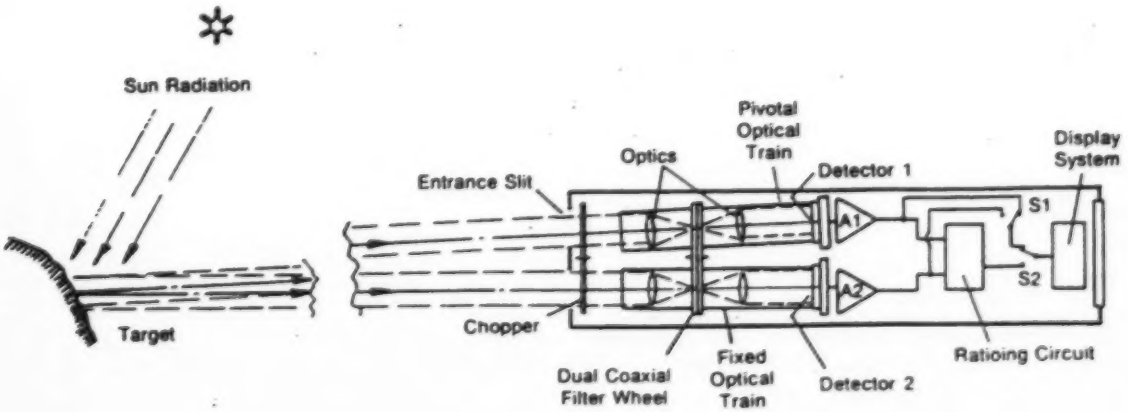
In U.S.A.
Barringer Geoservices Inc.,
15000 West 6th Avenue
Suite 300
Golden, Colorado 80401
Telephone: 303-277-1687
Fax: 303-277-1689

Selected Bibliography

1) Hunt, Ashley, 1979 Econ. Geol. 74, 1615-1629.
2) Hunt & Salisbury, Modern Geology, 1970. 283-300; 1971, 23-30, 195-205; 1973, 85-106, 217-224, 237-244; 1974, 15-22; 1976, 211-217.
3) Hunt, 1977, Geophysics, No. 3, 501-513.
4) Hunt, 1979, Geophysics 44, No. 12, 1974-1986.
5) Goetz and Rock, 1983, Economic Geology 78, No. 4, 573-590.
6) Gladwell, Lett and Lawrence, 1983, Economic Geology 78, 699-709.

SPECIFICATIONS:

RADIOMETER HEAD	
Spectral Range:	0.4 - 2.8 micrometres (μ).
Filters:	Not included. To be selected from available stock or custom ordered, Barringer will make a preliminary filter evaluation for any customer application. Filters as narrow as 1nm are available in the spectral range of .4 to 2.5 μ.
Light Sources:	Scattered solar radiation, or artificial source.
Optics:	Standard unit has a 2° x 12° FOV. Common FOV selector for 1 meter target or distant targets.
Noise Equivalent Reflectance:	1.5% @ 1 sec. response time and 60° solar zenith angle.
Dynamic Range:	Typically three orders of magnitude of recordable signal within noise limit for each channel. Ratio range is 0 to 19.999.
Response Time:	Selectable 1 second or 5 seconds; can be modified to suit customer requirements.
Display:	Reflectance ratio, or individual radiometer signal, or battery voltage or detector temperature on 3.5 digit LCD.
Analog Outputs:	Reflectance ratio signal and radiometer outputs: 0 to 10 VDC at 10 k output resistance.
Mechanical:	Size — 4" x 5.5" x 9" (10cm x 14 cm x 24 cm) approximate Weight — 6 lbs (2.8 kg) approximate Pistol grip handle, shoulder strap, built in tripod adaptor (¼-20)
Environmental:	Ambient temperature range: 0 to 40°C (adjustable 10°C lower or higher) Dust sealed, splash and rain proof.
Power Requirements:	+ 6V DC: (8 hours operation from battery pack).
BATTERY PACK:	Belt mounted 6V rechargeable pack. 2" x 5" x 7" (5 x 13 x 18 cm) 4.5 lbs (2 kg).
REFLECTANCE TARGET PACKAGE:	Non water absorbing standard reflectance sample, belt mounted. 1" x 4.5" x 12.5" (2.5 x 11.5 x 32 cm) 1 lb. (0.5 kg).
SHIPPING/CARRYING CASE:	16" x 20" x 9" (41 x 51 x 23 cm), 12 lbs (5.5 kg) net.
OPTIONS:	A wide range of options available to suit individual requirements. A list of standard and stock filters is available.



Ratioing Radiometer Simplified Schematic.

Barringer reserves the right to make changes for the purposes of product improvement.

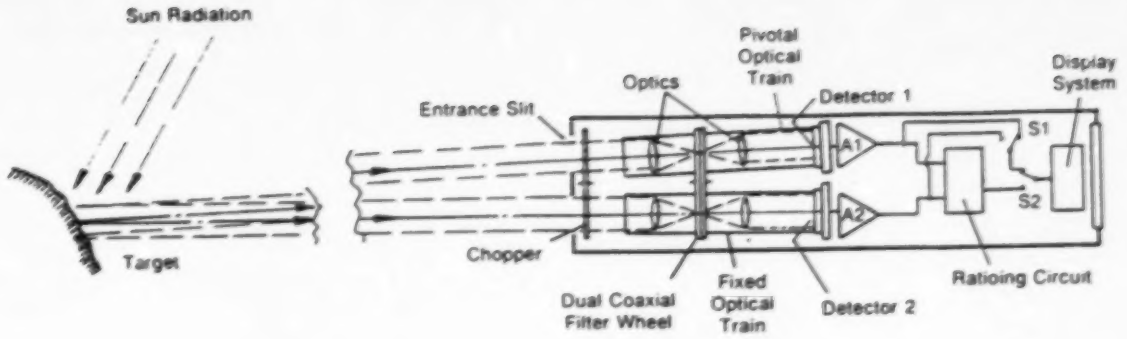


Fig. 1
Ratioing Radiometer Simplified Schematic.

Current research has shown that calibration curves may be constructed for a variety of minerals. A selection of these calibrations are shown on Fig. 2. Such calibration curves allow for semi quantitative field and laboratory estimation of mineral abundance. Typical detection limits are of the order of one modal percent. The precision of these determinations is at the 99 percent confidence level as determined on sixty replicate sample orientations of a selection of typical rock samples. Further research has concentrated on studies of alterations surrounding several Ontario gold occurrences.

The early Precambrian gold deposits of the Kerr Addison Mines located in the Southern part of the Abitibi or Agenic Belt, Ontario consist of three types. They are, in order of importance (A) "Flow Ore", a pyrite rich extrusive Basalt (B) "Carbonate Ore", a fuschite bearing quartz carbonate rock; (C) "Albitite Ore", discrete albite rich dykes. Most rocks include andesitic pillow breccia, talc carbonate, talc schist, sediments and Mg-Tholeiite of Timiskaming age. The green carbonate ore contains dolomite as the principal carbonate phase which is replaced in importance by calcite with distance. The MgO/CaO ratio indicates this change with erratically high ratios over the ore zone (Fig. 3).

H.H.R.R. Calibration Curves for Selected Minerals in Quartz Matrix

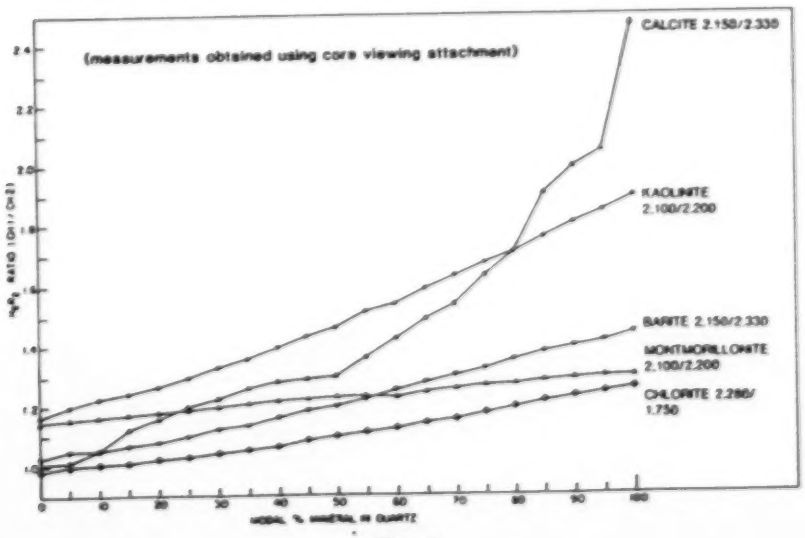


Fig. 2

BARRINGER RESEARCH

HAND HELD RATIOING RADIOMETER application release No. 1: The use of the HHRR for mineral exploration:

HAND HELD RATIOING RADIOMETER:
Spectral identification and classification of a mineral target.

An important application of the Barringer Hand Held Ratioing Radiometer is the identification of different hydrothermal alteration mineral assemblage in outcrop, hand specimens and drill core samples. The instrument is designed to identify mineralogical variation based on optical analysis of reflected artificial or natural light from targets down to one centimetre by five centimetres in size.

The instrument is a self-contained, dual beam ratioing radiometer with two optical trains directed at the same target. It provides a continuous digital readout of ratio values from the two optical trains each of which includes a separate filter for selection of the narrow spectral bands to be ratioed for identification of the presence of a particular target, on the basis of known spectral characteristics of the target.

Positive target identification can be achieved by measuring the ratio of the two most prominent spectral peaks characterizing the target. The instrument can provide a selective ratio of such spectral peaks in any of up to 25 pairs of pre-selected narrow bands in the spectral range from 0.4 micrometres to 2.5 micrometres.

Fig. 1 is a simplified schematic of the Hand Held Ratioing Radiometer showing the method by which the instrument provides a reading of the spectral characteristic of the chosen target.

The radiometer is simple to operate with minimal skill required. Field calibration is carried out infrequently with solar radiation or an artificial source, such as a quartz-iodine lamp and a highly reflective reference material having a uniform spectral reflectance in the region of interest.

The portable radiometer system comprises the Ratioing Radiometer Head, a Battery Pack, a Battery Charger, a Standard Reflectance Target Package, and a carrying case. Sets of Narrow Band Filters are available to suit a wide variety of applications.

More recently a small attachment has been developed which enables measurements to be made on diamond drill core.

Both flow ore and albitite ore are enriched in Na and Zr and depleted in CO, Ni and volatiles compared to adjacent rocks.

In addition Flow Ore is enriched in Ti, Mn, and Cu and depleted in K and Ti. The albitite ore shows moderately enhanced levels of Sr and Th. Green carbonate ore is enriched in K, Mg, Co, ±V, ± Zn, ± Ni and depleted in Al, Ca and Ti compared to nearby lithologies.

The results of the HHRR survey (Fig. 4) show a broad carbonate haloe around the ore bearing horizons. Since carbonate minerals are not common in unaltered Mg-Tholeiite a 600 metre carbonate alteration haloes is inferred to be present around the ore itself. The bound-water sensitive ratio shows anomalous values within the mineralized zone, probably indicating the increasing presence of fluid inclusions in the mineralized zone due to hydrothermal alteration processes.

H.H.R.R. Survey of Kerr Addison Mine (3850 level)

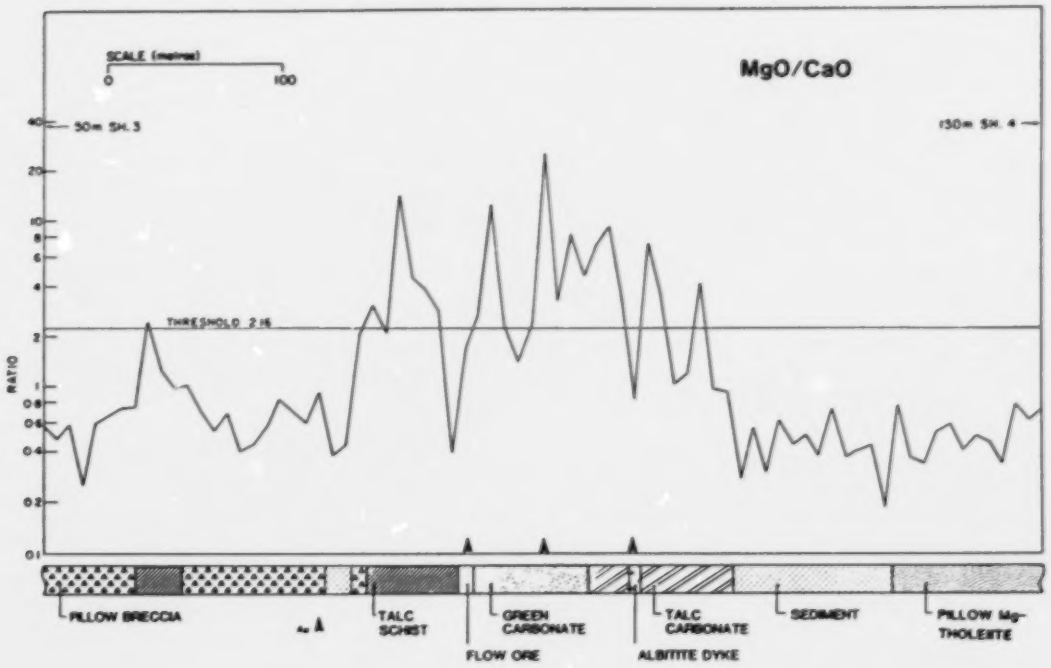


Fig. 3

POTENTIAL APPLICATIONS:

In addition to the obvious capability of rapidly logging large quantities of diamond drill core for alteration cones at a fraction of the time and cost of geochemical techniques, other potential applications include:

- Basal till sample mineral evaluation
- Stream sediment mineral evaluation
- Discrimination between "Pregnant" gossan and barren ironstone exposures.
- General detection of geochemical alteration haloes
- Hydrothermal alteration pattern
- Diamond drill core logging
- Oil well drill core logging

H.H.R.R. Survey of Kerr Addison Mine (3850 level)

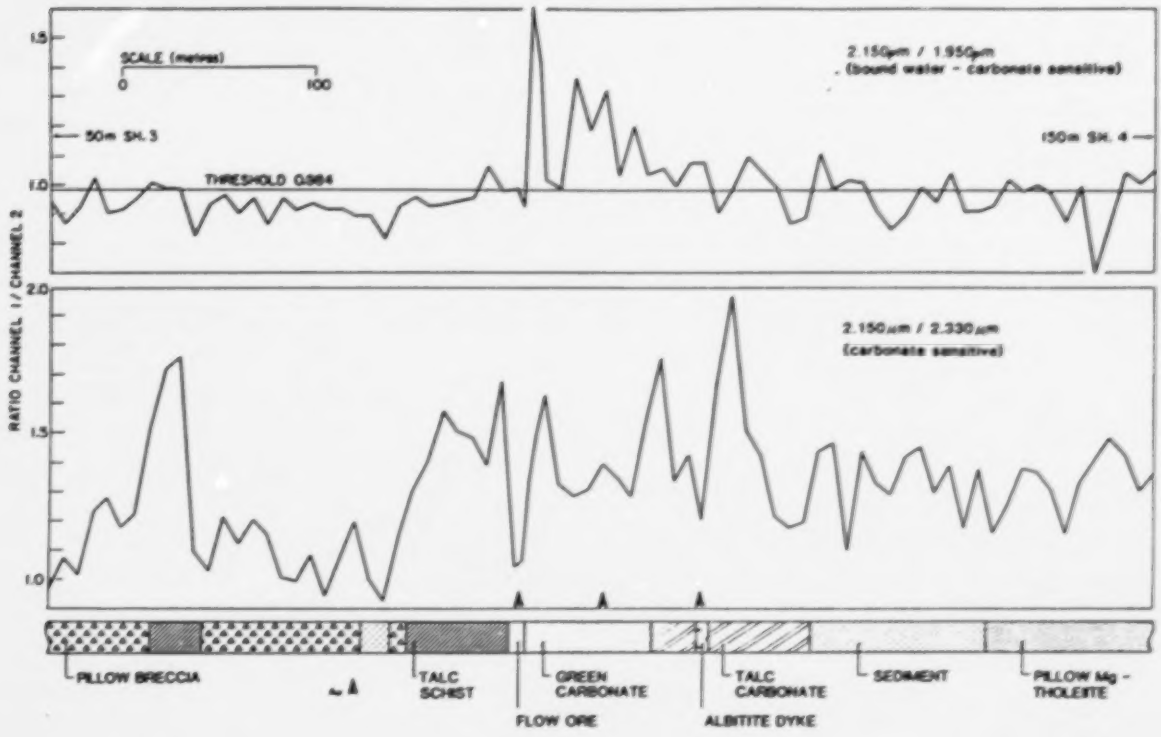


Fig. 4

In the past several months, extensive research has been performed by Barringer, on the applications of the Hand Held Ratioing Radiometer. Barringer staff will be pleased to discuss the results of this research and/or supply additional documentation pertaining to the various applications of the radiometer.

A demonstration of the radiometer can also be arranged, by request, from our Toronto office.

For further information contact:

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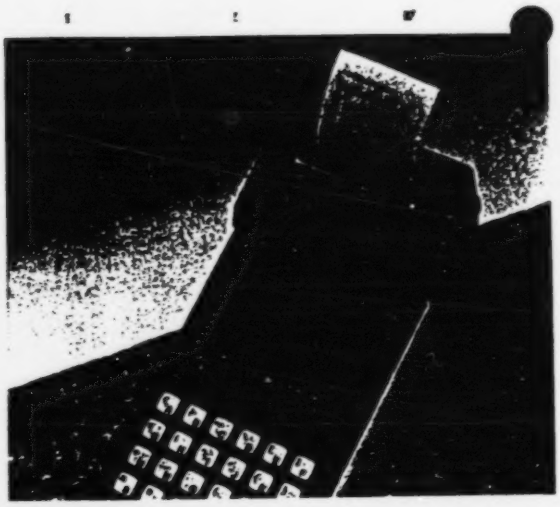
Telex: 06-989-183
Cable: Baresearch

Barringer Resources Inc.
1626 Cole Blvd.
Golden, Colorado 80401
U.S.A.
Telephone: (303) 232-8811
Telex: 45810

MICROFLEX PC1000



SPECIFICATIONS

MEMORY:	ROM: 128K System Memory CMOS. Standard Configurations: 96K – 128K – 256K – 384K – 640K Disk Storage CMOS. Virtual Disk Memory Configurations: 192K – 512K – 640K – 896K – 896K Video Memory: 32K
OPERATING SYSTEM:	MS-DOS® Version 2.25 (equivalent to 3.2 without network) ROM Resident IBM™ PC Compatible ROM BIOS
MICROPROCESSOR:	80C88, CMOS – 4.9152 MHz
INTEGRATED CLOCK:	Year/month/day/ hours/minutes/seconds
DISPLAY:	LCD, dot-matrix 128 × 128 pixels, CGA compatible Upper and lower case, graphics 16 lines of 16 or 21 characters Programmable angle of vision Supertwist® Optional
KEYBOARD:	47 multi-functions keys Numerical pad Audible feedback Programmable Customized keyboard: optional
POWER SUPPLY:	Module of 6 AA type rechargeable batteries Separate ramdisk and clock backup batteries
INPUTS/OUTPUTS: **2 DB-15 CONNECTORS**	1 RS232 SERIAL PORT, IBM™ PC compatible 1 serial port, TTL level 7 Digital TTL signals (5 outputs, 2 inputs) 2 analog inputs: 0 to 5 volts, 8 bits of resolution
COMMUNICATION:	Communication protocol integrated Bidirectional, CRC error detection 300 to 38,400 bauds, direct connection 300 to 2,400 bauds with modem
CASING:	Polycarbonate/polyester, injected mold
DIMENSIONS:	Height: 2.1" (54 mm) Width: 4.4" (111 mm) Length: 10.4" (264 mm)
WEIGHT:	With batteries: 2.4 lb/1.1 kg
TEMPERATURES:	Operating: – 4°F to + 122°F (– 20°C to + 50°C) Stockage – 40°F to + 158°F (– 40°C to + 70°C) Humidity: 95% non condensing
CHEMICAL RESISTANCE:	Aromatical hydrocarbones, ketones, hydroxides, acids, alcohols, mineral essences, glycols, organic solvents, oils and others
PERIPHERALS:	Modular printer: 24 or 42 characters Portable printer Portable disk drive (serial) Bar code reader: Optical or Laser Forestry scaler, Electronic caliper, Concentrator
EMI/RFI	FCC, Class A

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GENEQ inc.

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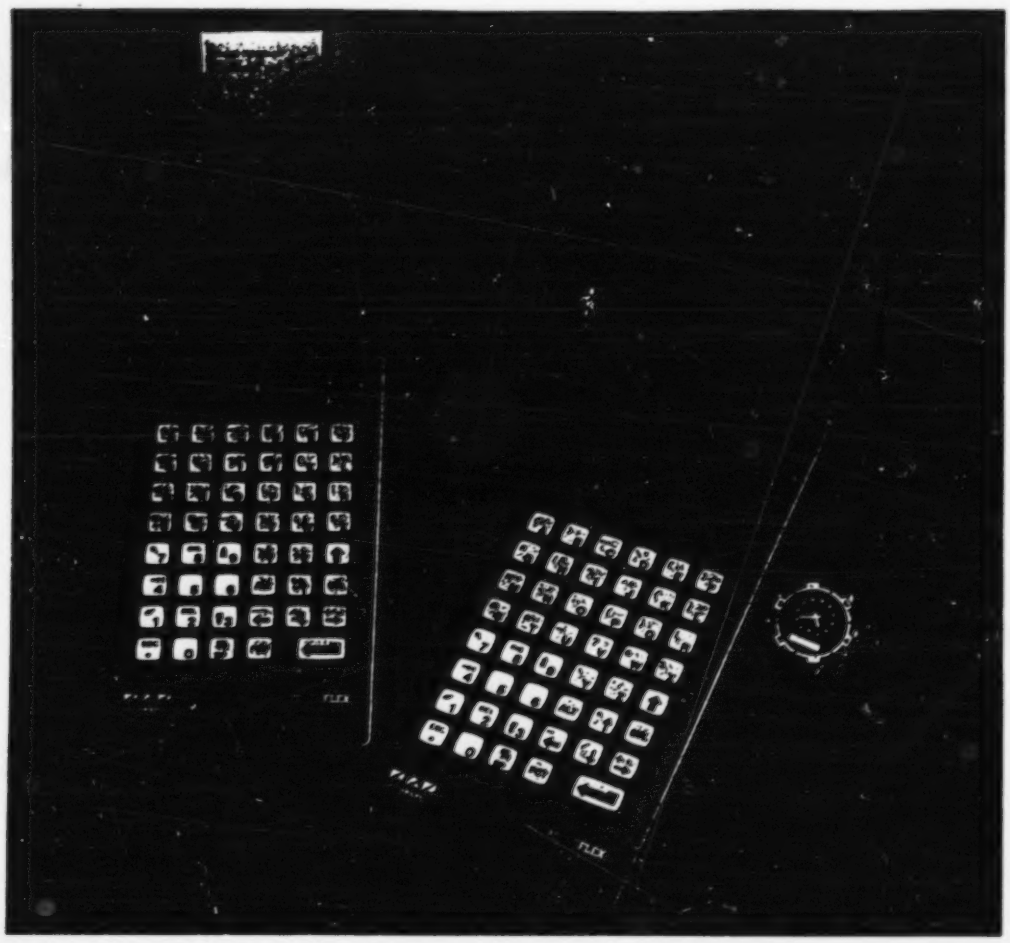
MICROFLEX PC1000



D.A.P. TECHNOLOGIES is changing forever the way the world thinks of **hand-held micro-computers**.

Introducing the MICROFLEX® PC 1000; our latest technical achievement provides you with desktop power that fits in the **palm of your hand**. Like your IBM™ PC or compatible, its operating system is **MS-DOS®** using an 80C88 microprocessor. This compatibility allows you to upload and download programs through the standard RS-232 port via cable or a Hayes compatible modem to any **MS-DOS®** desktop, at speeds up to 38,400 bauds.

Its **flexibility** permits you to program in a standard **MS-DOS®** environment using languages such as DBASE, Pascal, BASIC, C, COBOL, etc., or the use of other existing software.

The MICROFLEX® PC 1000 used for **data collection** is especially designed for **mobile people** working in adverse weather conditions requiring a **rugged all weatherized hand-held micro-computer**, where you would not risk using your desktop or laptop.

This **small miracle** weighing 2.4 lb [1.1 kg] batteries included, will withstand a 4-ft [1.21 m] drop onto concrete.

The MICROFLEX® PC 1000 comes in five standard memory configurations: 288K - 640K - 896K - 1.2 Meg and 1.5 Meg. Its keyboard features 47 standards keys with multi-function numerical and alphabetical separate keys with audible feedback. Sealed to keep out **dust, humidity and water**, it will operate in extreme temperatures of −4°F to +140°F [−20°C to +60°C.].

Its highly readable LCD (Liquid Crystal Display) allows **16 lines of 16 or 21 characters**, with graphic capabilities and programmable angle of vision. Accessories and peripherals may be connected to the MICROFLEX® PC 1000 via DB-15 connectors.

The cost effectiveness and reliability of the MICROFLEX® PC 1000 make it a must for **mobile people** working in Industrial, Scientific and Commercial fields such as in Inventory and Delivery of Products, Meter Reading, Law Enforcement, Medical and Health Care, Forestry, Military, Land Surveying, Mining, Route Management, Agriculture and Field Service, etc.

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Available Modules:

Model No.	Voltage Range	Accuracy
DAPAFAD-01	0-4.5 V	1 m
DAPAFAD-02	0-45 V	10 m
DAPAFAD-03	0-450 V	100 m
DAPAFAD-04	0-4000 V	1 V

Ranges are software selectable

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GENÉQ inc.

15 Bit Analogue to Digital Converter For The Dap Microflex PC1000

Description:

Now available for the Dap Microflex PC1000 is an external A to D conversion module that slides onto the top end of the PC1000. The Module has an LCD screen which is user controllable. It can display messages, or the measured values, in one of three selectable sizes. Backlighting is also available.

Data is transferred by simply turning on a switch. The transmission is verified by an indicator light, which is controllable by the digital output (pin 12) of the PC1000.

Technical Specifications:

1. Channels: 7 single-ended analogue inputs
2. Resolution: 15 bits
3. Scanning Speed: 20 scans/sec
4. Display: 4 lines, 20 columns, alphanumeric
   selectable lettering size (small, medium, large)
   Backlit (optional)
5. Validation Button with indicator light
6. Programming: Basic, DBase, C languages
   programmable via the communication port com 2
7. Cold junction reference for thermocouples
8. Multimeter capability
9. Consumption: 5mA in operation
   400 µA in standby

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□ 7978 JARRY E., MONTRÉAL, QUÉBEC CANADA H1J 1H5 TÉL.: (514) 354-2511 TÉLEX: 05-829568
MTL. FAX: 514-354-6948

Economic Geology
Vol. 78, 1983, pp. [illegible]

Application of Reflectance Spectrometry to Mineral Exploration Using Portable Radiometers

D. R. GLADWELL, R. E. LEFT, AND P. LAWRENCE

Barringer Magenta Ltd., 304 Carlingview Drive, Rexdale, Ontario M9W 5G2, Canada

Abstract

The operating parameters of the Barringer hand-held reflectance radiometer[1] are described and examined in detail. The use of reflectance spectrometers as backup instruments for radiometer filter selection is investigated by generating laboratory spectra of pure minerals, mineral mosaics, and lithogeochemical hand specimen and drill core samples. Alteration halos around two areas of gold mineralization in the Abitibi orogenic belt, northern Ontario, are distinguished based on carbonate, bound water, and clay mineral-sensitive filter selections.

Introduction

ANALYSIS of solar reflectance spectra obtained using broad band (half-band pass of greater than 30 nm) interference filters has been extensively employed as a remote-sensing method for mapping regional geology and identifying large hydrothermal and geothermal patterns (Rowan and Kahle, 1982; Sadowski and Abrams, 1982). Moreover, the feasibility of routine remote identification of specific alteration minerals has been demonstrated using airborne high-resolution spectroradiometers (Goetz et al., 1982; Collins and Chang, 1982). These workers have, however, stressed the need for in situ ground measurements of reflectance to allow accurate calibration of the remote-sensing data. The recent development of small, portable reflectance radiometers, such as the instrument described in this work, enables rapid in situ confirmation of geologic and geobotanical features identified by remote-sensing techniques.

Most previous spectral reflectance studies of geologic materials have concentrated on generating complete visible to near-infrared spectra of pulverized, homogenous, and generally unaltered rock and mineral samples. For example, Hunt and Salisbury (1970, 1971) and Hunt et al. (1971, 1973a) determined reflectance spectra from 0.4 to 2.5 μm for most common rock-forming silicate, oxide, carbonate, and sulfate minerals. Similarly more recent research has focused on establishing spectra for different rock types in addition to constituent minerals (Hunt et al., 1973b and c, 1974). Hunt and Ashley (1979) recorded the visible and near-infrared spectra for a suite of hydrothermally altered rocks representing silicic, argillic, phyllic, and propylitic alteration types.

The objectives of this study are: (1) to examine in detail the operating parameters of the Barringer hand-held reflectance radiometer and the use of the Barringer reflectance spectrometer[2] as a backup instrument, and (2) to assess the practical use of the radiometer in delineating alteration halos around two areas of gold mineralization in northern Ontario.

Instrumentation and Methodology

Radiometer design

The Barringer radiometer is designed to measure reflected light energy from a target in two narrow passbands, selectable in the 400- to 2,500-nm range. The selectable instrument output (liquid crystal digital display and analogue output) provides the power through each passband (channel) and the ratio of the two channel outputs (channel 1/channel 2). The design of the instrument is shown schematically in Figure 1. The instrument has an optical train for each channel which may be focused for optimum instrument performance at 1 m or at >10 m from the target. After passing through a chopper, which modulates the incoming dc-reflected energy for both channels, the light is focused onto, and a portion passes through, a filter selected by the operator, after which the light is refocused onto a thermoelectrically cooled PbS detector. The design of the radiometer is fully discussed by Daubner et al. (1981).

Spectrometer design

The Barringer spectrometer is designed to measure the light energy reflected from any target in a 90-s scan of the 458- to 2,409-nm wavelength region. It has a spectral resolution of 1.5 to 4 nm, is portable in the field, and is designed to compensate automatically for changes in the brightness of the incident radiation. The design (Fig. 2) includes a chopper to

[1] Developed by staff members of the California Institute of Technology at the Jet Propulsion Laboratory during research sponsored by NASA. Manufactured and sold by Barringer under exclusive license from the California Institute Research Foundation.

[2] REFSPEC™.

0361-0128/83/166/699-12$2.50

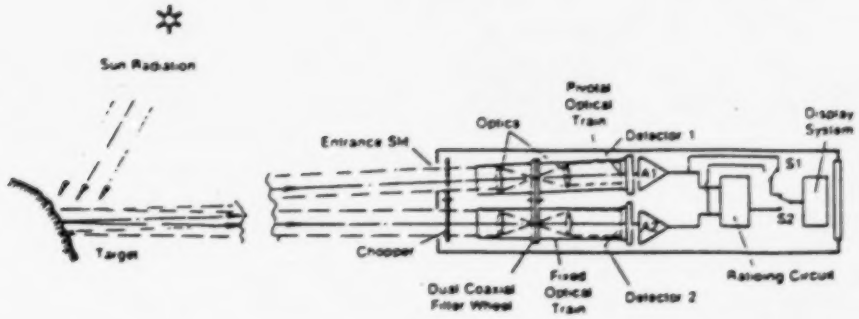

FIG. 1. Simplified schematic of the Barringer hand-held reflectance radiometer

control the sequential input of target light, light reflected from a barium sulfate-painted surface, and then light reflected from a black metal surface to a scanning, grating monochromator. The latter two reflectance standards are illuminated by light emerging from the integration sphere. Two different detectors and five filters are used at the appropriate intervals to record the entire spectrum in five regions. The detector output for the black surface is subtracted from each of the target and downwelling solar radiation signals, and the ratio of the two subtracted signals is calibrated using an external barium sulfate reflectance standard to give a direct measurement of target reflectance. The design and operational features of this spectrometer are fully described by Davies et al. (1981). Its target-viewing distance for all spectral measurements was 9 cm.

Radiometer measurement technique

Prior to target reflectance measurement the gain of each channel was manually adjusted to within the operating range of the instrument. This was achieved by balancing channel outputs (ratio output of unity) with a target of Fiberfrax.[3] The majority of the data was acquired indoors using a calibrated (W cm^{-2} nm^{-1}) lamp powered through a voltage regulator and a Variac. The lamp was tested for current draw stability over time. The lamp and the radiometer were mounted on sturdy tripods to facilitate modification and measurement of lamp-target-radiometer geometry.

[3] Fiberfrax is the trade name of a nonasbestos insulating material manufactured by the Carborundum Company. It has a high spectrally diffuse reflectance in the visible and near-infrared

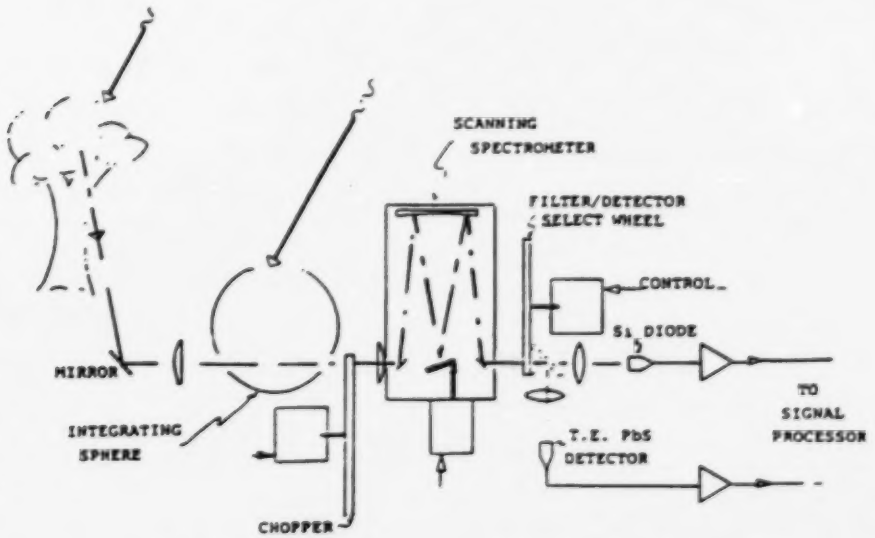

FIG. 2. Simplified schematic of the Barringer reflectance spectrometer (REFSPEC™)

To facilitate data acquisition and reduction using available software, during laboratory experiments the analogue outputs for channel 1, channel 2, and the ratio were wired via coaxial cable to a four-channel Hewlett Packard 59313A analogue to digital converter and then to a Hewlett Packard 85 desk top computer and were subsequently recorded on magnetic tape.

Radiometer Operating Parameters

Instrument stability

The objectives of these experiments were to measure the stability of the lamp and the radiometer, and to quantify the noise level of the radiometer.

The standard lamp stability was tested by leaving it on for six hours at a current of 8 A. The current drawn by the lamp gradually decreased by 0.5 percent, indicating a change in light intensity of <1 percent.

The stability of the radiometer was measured under the light conditions described above using the standard 6-V, 7.5-A hour battery as the power supply and a target of Fiberfrax. A group of 30 readings were taken every 30 min for a total period of 16 h. The battery power supply was recharged during measurement for 3 h. The radiometer's channel signals changed by a total of 4 percent over the 16-h period.

The noise levels of the radiometer were monitored at seven light intensities over the full instrumental range using a Fiberfrax target. Lamp voltage was varied at monitored increments using a Variac. Since the error distribution at a given illumination level for each channel was of interest, accompanying changes in illumination color temperature were not monitored. At the 99 percent confidence level the mean error on a signal between 1.010 to 0.249 V was 0.3 percent of signal strength. The maximum observed error at this confidence level was 0.5 percent of signal strength.

Field of view evaluation

The objective of these measurements was to establish the field of view of each channel of the radiometer. This field of view was examined by setting the instrument 1 m away from a point light source and recording channel response with the light source at all intersections of a 1.2-cm grid. Filters were selected as for the stability test discussed above. The data indicate that the field of view of channel 1 is offset 2 cm to the left of that of channel 2 and that both are approximately 28 × 4 cm in dimension. Since this area is larger than the target size of many geologic samples (e.g., diamond drill core), an optical device was designed, assembled, and tested to reduce the field of view. The modified field of view was remeasured with a radiometer target distance of 30 cm and a grid spacing of 0.5 cm. Modified data revealed an approximate coincidence of the field of view of channels 1 and 2 with field of view dimensions of 8 × 1 cm. A practical advantage of the optical device is that it can be quickly attached to the radiometer for measurement along diamond drill core.

Dynamic range, linearity of response, and angle of view measurements

The objectives of these tests were to determine if reflectance ratios are affected by (1) changing brightness of incident radiation, (2) changing light source-target radiometer geometry, and (3) changing target particle size in combination with these factors. The results of changing the brightness of the incident radiation are given in Table 1, and the results obtained by changing the other parameters in combination are given in Table 2. It is clear from the data that there is little change in the ratio obtained for powdered target types for both changes in incident light brightness and radiometer-target geometry. However, ratio changes are apparent for both tests for coarse-grained (2–4 cm) target types. The ratio changes observed for coarse-grained targets are thought to be mainly caused by shadow effects.

Inherent polarization effects

All surfaces cause some polarization on reflectance. Hitherto, measurements of reflected radiance have generally been made with radiometers in which the question of polarization has been ignored (M. J. Duggin, pers. commun., 1981). An experiment was there-

TABLE 1 Radiometer Ratio Changes with Decreasing Incident Light Brightness for Four Target Types

Target-radiometer distance (cm)	Target	Channel 1 / channel 2
50	Fiberfrax	1.000
81	Fiberfrax	1.011
100	Fiberfrax	1.011
123	Fiberfrax	1.005
50	Alunite (coarse)	0.502
81	Alunite (coarse)	0.560
100	Alunite (coarse)	0.551
123	Alunite (coarse)	0.515
50	Pyrolusite (coarse)	0.958
81	Pyrolusite (coarse)	0.949
100	Pyrolusite (coarse)	0.796
123	Pyrolusite (coarse)	0.913
50	Pyrophyllite	1.100
81	Pyrophyllite	1.093
100	Pyrophyllite	1.108
123	Pyrophyllite	1.058

TABLE 2. Radiometer Ratio Changes with Decreasing Radiometer-Target Angle for Seven Target Types. Targets were unpacked

Target	Radiometer-target angle (°)[1] (Radiometer-target distance, 1 m)	Channel 1/ channel 2
Filterfrax	90	0.997
Filterfrax	70	0.999
Filterfrax	60	1.004
Microcline (coarse)[2]	90	1.001
Microcline (coarse)	70	1.013
Microcline (coarse)	60	1.003
Microcline (powder)[3]	90	0.993
Microcline (powder)	70	0.987
Microcline (powder)	60	0.990
Kaolinite (coarse)	90	1.181
Kaolinite (coarse)	70	1.147
Kaolinite (coarse)	60	1.156
Kaolinite (powder)	90	1.125
Kaolinite (powder)	70	1.126
Kaolinite (powder)	60	1.125
Calcite (coarse)	90	2.610
Calcite (coarse)	70	2.748
Calcite (coarse)	60	2.852
Calcite (powder)	90	1.317
Calcite (powder)	70	1.326
Calcite (powder)	60	1.324

[1] The lamp was normal to the target plane and 1.1 m from the target.
[2] Coarse grains were from 2 to 4 cm in diameter.
[3] Powdered samples were pulverized to less than 0.075 mm.

fore designed to examine the inherent polarization of the radiometer.

There are two possible sources of inherent polarization in the radiometer: the interference filters and the alumina covers protecting the PbS detectors. The inherent polarization caused by these items was examined by allowing white, unpolarized light to pass through a rotatable Carl Zeiss Jena polarizer prior to entering the radiometer. The following measurements were then taken with the field of view reducer removed: (1) with a fixed filter (560 nm) position the angle of the polarizer was increased in increments of 45° from 0° to 360°, for both channels independently; and (2) with a fixed polarizer position the filter (560 nm) was rotated through 360° at 45° increments.

The data obtained (Table 3) reveal maxima and minima at 90° intervals when the polarizer is rotated below channel 2 (total polarization effect is 4.1%); these intervals are absent for the similar test on channel 1. The absence of a polarization effect for channel 1 indicates that the optic axis of the uniaxial alumina cover is aligned with the optic train whereas the optic axis of the uniaxial alumina cover in channel 2 is at an angle to the optic train. For this reason the test of inherent polarization of the (560 nm) filter was carried out using channel 1. The results (Table 3B) show a single minima at a rotation of 180° which cannot be a polarization effect and thus is inferred to be caused by an inhomogeneous filter coating.

Inherent polarization effects caused by the borosilicate glass lens used in the field of view reducer and the quartz windows on the entrance slits were not examined since these items are constructed from fused glass and silica, respectively.

Examination of Geologic Materials

The complex reflectance spectra of natural rocks are due to the interaction of the spectra of component minerals (Hunt et al., 1973b). Furthermore, the abundant rock-forming minerals are not usually responsible for the diagnostic spectral features of rocks (Hunt and Ashley, 1979). For these reasons laboratory spectra, obtained using the Barringer spectrometer, of 54 mineral specimens were measured as described above. A selection of these minerals was analyzed for purity both chemically and by XRD.

Radiometer calibration curves and detection limits for various minerals

Chlorite, montmorillonite, barite, kaolinite, and calcite were added separately in increments of 5 modal percent to sand-size (0.15–0.63 mm) quartz matrices, and changes in the reflectance spectra were observed

TABLE 3. Measurement of Radiometer Polarization at 560 nm

Polarizer angle (°)	Channel 1 (V)	Channel 2 (V)
A. Inherent polarization caused by alumina covers		
0	0.268	0.245
45	0.269	0.246
90	0.269	0.243
135	0.269	0.235
180	0.268	0.240
225	0.265	0.241
270	0.265	0.241
315	0.269	0.239
360	0.266	0.243
B. Inherent polarization caused by filters		
0	0.230	
45	0.235	
90	0.230	
135	0.226	
180	0.214	
225	0.215	
270	0.222	
315	0.239	
360	0.229	

using the spectrometer and radiometer. Reflectance spectra of the chlorite, barite, montmorillonite, kaolinite, and calcite in the 1.1- to 2.4-wavelength range are given in Figure 3, and chemical analyses of the quartz, montmorillonite, and kaolinite samples are presented in Table 4.

The calibration targets were constructed in the following manner. A 5-mm layer of the sand-size quartz grains was placed 30 cm from the radiometer, which observed the target vertically. The calibrated lamp illuminated the target at an angle of 15° from vertical. The layer of quartz sand was smoothed gently in order to obtain a flat surface. Using the measured field of view data for the radiometer's optical attachment (discussed above), a mask was constructed with an aperture representing 5 modal percent of the field of view. With the mask placed temporarily on the layer of quartz, an increment of the mineral was deposited on the quartz surface to a depth of 4 mm. The target so constructed was viewed by the radiometer after removal of the mask, with appropriate filters inserted, and also by the spectrometer. Since the viewing and illumination angles were close to vertical, the difference of 4 mm in height between the quartz layer and the mineral patch was not considered to affect the calibration. Subsequent increments of mineral were added to the quartz layer in a symmetrical fashion. The calibration curves generated were checked by reversing the above procedure (i.e., adding quartz increments to a layer of the mineral).

TABLE 4. Chemical Analyses of Selected Minerals Used to Construct Calibration Curves

Element[1]	Mineral: Quartz	Montmorillonite	Kaolinite
		percent oxide	
Al_2O_3	0.075	0.072	25.300
Fe_2O_3	0.008	0.092	0.852
CaO	0.023	7.820	0.002
MgO	0.026	28.000	0.064
TiO_2	0.028	0.012	1.610
MnO	b.d.	0.127	0.002
Na_2O	0.026	0.309	0.114
K_2O	b.d.	0.270	0.110
P_2O_5	b.d.	0.050	0.080
		ppm	
Be	b.d.	b.d.	2
Cd	b.d.	b.d.	b.d.
Cr	b.d.	11	63
Co	214	29	5
Cu	8	b.d.	14
Pb	5	b.d.	40
Ni	5	35	33
Sr	1	248	46
Th	b.d.	25	13
Zr	b.d.	4	52
V	2	10	58
Zn	b.d.	22	50
Mo	b.d.	b.d.	b.d.
Ag	b.d.	b.d.	b.d.

[1] Analysis by HF digestion and nebulization into an inductively coupled argon plasma.
b.d. = below detection.

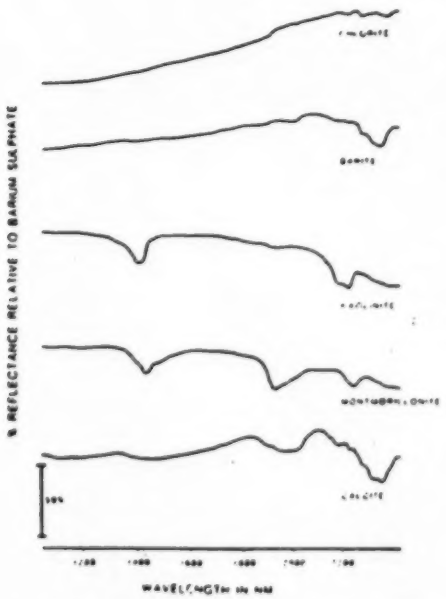

FIG. 3. Near-infrared spectra of chlorite, barite, kaolinite, montmorillonite, and calcite specimens used to construct calibration targets.

The filters of the radiometer were chosen such that the channel 1/channel 2 ratio increased with increasing mineral content. The filters selected for each calibration are given in Table 5. No attempt was made, at this stage of the research, to select filter combi-

TABLE 5. Filter Combinations (Channel 1/Channel 2) and Estimated Detection Limits for Five Modal Percent Mineral Radiometer Calibration Curves

Mineral	Filters used (nm)[1]	Mean ratio at zero concentration	Detection limit[2] (modal %)
Calcite	2.150/2.330	0.979	1
Barite	2.150/2.330	1.028	5
Chlorite	2.280/1.750	0.989	2
Kaolinite	2.100/2.200	1.169	1
Montmorillonite	2.100/2.200	1.148	2

[1] All filters had a half band-pass width of approximately 30 nm.
[2] Detection limits are rounded to one significant digit.

FIG. 4. Near-infrared spectra of selected calcite calibration targets. ▲ = center wavelengths of channel 1 and channel 2 filters.

nations which were uniquely sensitive to the presence of a given mineral.

The filters chosen for the calcite and barite calibrations were a reference filter at 2.15 μm in channel 1 and a 2.33-μm filter in channel 2. With increasing content of these two minerals, an absorption feature develops at approximately 2.33 μm and intensifies with increasing mineral content. Selected spectra of the calcite calibration (Fig. 4) illustrate this process. Filters were chosen for the kaolinite and montmorillonite calibrations at 2.1 μm in channel 1 and 2.2 μm in channel 2. Figure 5 shows the spectral changes occurring with increasing montmorillonite content of the calibration target.

Filters for the chlorite calibration were chosen at 2.28 μm in channel 1 and 1.75 μm in channel 2. Figure 6 shows the spectral changes occurring with increasing modal percent chlorite. The absorption feature near 2.3 μm caused by hydroxyl ions was not used for the calibration as it is relatively subdued in this chlorite sample (cf. Hunt and Salisbury, 1970). The spectra shown in Figure 8, below, however, reveal the development of a general increase in spectral slope toward shorter wavelengths with increasing chlorite content. This change in slope is due to intensification of the broad ferrous iron electronic absorption feature at approximately 1.1 μm. As discussed above, it is important to note that the filter combination selected is not uniquely sensitive to chlorite. The presence of any mineral containing ferrous iron (e.g., jarosite) will cause a ratio change. Furthermore, the 2.28 μm/1.75 μm ratio will not be sensitive to the presence of Mg-bearing chlorite and is sensitive to the presence of both alunite and gypsum.

The calibration curves obtained with the radiometer for chlorite, montmorillonite, barite, kaolinite, and calcite are presented in Figure 7. The results reveal that for all minerals except calcite a linear relationship exists between the ratio and modal percent of mineral in quartz. The calcite calibration is approximately linear to 80 modal percent, and then with increasing calcite content the curve increases in slope. Hunt and Salisbury (1971) report a carbonate absorption feature at 2.16 μm. The spectra (Fig. 4) show the development of this feature at extreme carbonate contents. Since the reference filter (channel 1) is positioned at 2.15 μm, the development of the 2.16-μm carbonate feature and its intensity relative to the 2.33-μm carbonate feature influences the calcite calibration curve.

The detection limits, defined as the mineral modal percent equivalent of the mean of 11 successive ratio measurements at zero modal percent mineral (pure quartz) plus three standard deviations, are given in Table 5, which also shows the filter combinations.

Examination of Rock Suites

Rock samples were collected at two gold-mineralized localities: the 3850 level of the Kerr Addison mine, Virginiatown, and a northern Ontario gold prospect (samples of drill core).

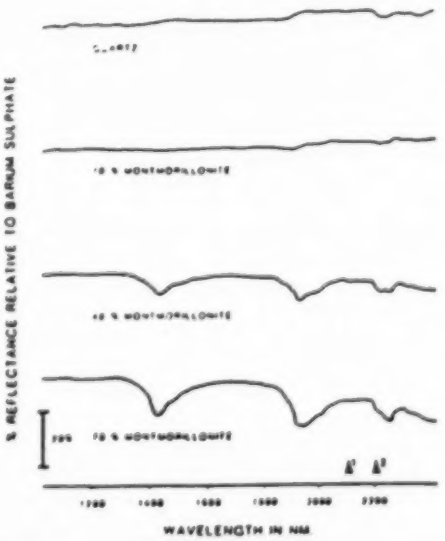

FIG. 5. Near-infrared spectra of selected montmorillonite calibration targets.

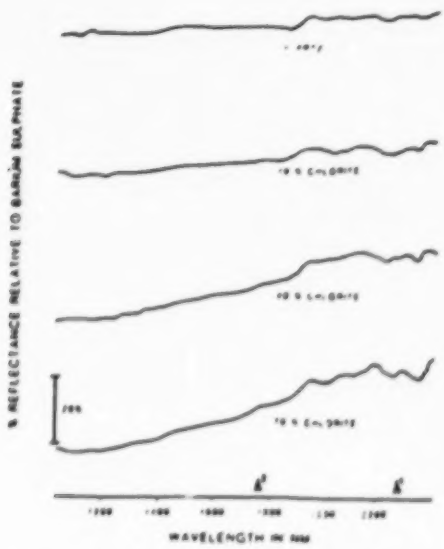

FIG. 6 Near-infrared spectra of selected chlorite calibration targets

In addition to radiometer monitoring the samples were subjected to whole-rock geochemical analysis, and the petrography of representative samples of each lithologic type was examined by transmitted light microscopy. Spectra of these selected samples were also generated. Filters for radiometer monitoring were selected based on the observed petrography and reflectance spectra.

Kerr Addison (3550 level) rock suite

Geology: The early Precambrian gold deposits of the Kerr Addison mine are located in the southern part of the Abitibi greenstone belt, Ontario. There are three types of gold ore, listed below in order of importance: (1) flow ore, a basaltic volcanic extrusive, rich in finely disseminated pyrite; (2) carbonate ore, a fuchsite-bearing quartz carbonate rock; and (3) albitite ore, discrete albite-rich bodies with sharp intrusive contacts with their quartz carbonate host rocks. The Larder Lake break is the most important structural feature in the mine itself, separating Timiskaming sediments from volcanics and tuff of the same age. The break consists of a 60-m-wide zone of carbonated schist and talc-chlorite schist along which some movement has taken place. The green carbonate ore contains dolomite as the principal carbonate phase which is replaced in importance by calcite with distance from the ore. Apart from carbonate minerals the only other alteration minerals found by petrologic observation were chlorite and chloritoid, the latter only present in sediments north of the break.

Light reflectance examination: Examination of the laboratory spectra revealed that two principal absorption features were common in the Kerr Addison rock samples at 1.95 and 2.33 μm. An additional absorption

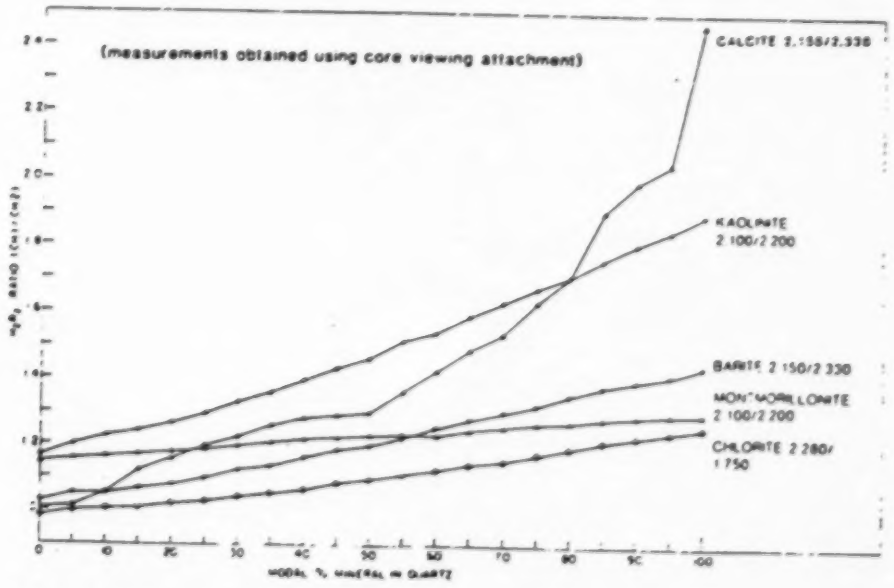

FIG. 7 Calibration curves obtained with the Barringer radiometer for selected minerals in a quartz matrix

feature at 2.2 μm was present in the spectra of some samples of the sediment near shaft 4. Petrologic examination of thin sections of the sediment showed that clay minerals were not present. The most likely source of this feature is therefore the brittle mica chloritoid which is present in amounts up to 15 percent in the sediment. Since the distribution of chloritoid was not related to the mineralization, only two filter pairs were used to delineate the ore zone: the 2.15 μm/2.33 μm pair and the 2.15 μm/1.95 μm pair. The response of these filter combinations to the absorption feature producing minerals present in the Kerr Addison rocks must be considered in some detail.

The 2.15-μm filter response is in general insensitive to all minerals present except for extreme carbonate mineral contents. The 1.95-μm filter response is sensitive to the presence of mineral-adsorbed water (e.g., chlorite, altered fuchsite, chloritoid). This wavelength is also susceptible to absorption by (free) atmospheric water. For this reason the 2.15 μm/1.95 μm ratio must be measured in the laboratory using an active light source. The presence of iron-rich chlorite would also contribute to absorption at this wavelength.

Since carbonate minerals are commonly present in the Kerr Addison rocks in excess of 40 modal percent, the major contribution to absorption at 2.33 μm is the carbonate absorption feature. However, both talc and chlorite (dependent on its composition) will also contribute towards absorption.

The results of the radiometer survey (Fig. 8) show a broad 2.15 μm/2.33 μm ratio halo around the ore-bearing horizons. As discussed above, in the context of Kerr Addison, this ratio predominantly reflects carbonate distribution. The talc-chlorite schist close to shaft 3 also shows high ratio values. Since this schist also has a high petrologically observed carbonate content, the high ratio values are a composite of talc, chlorite, calcite, and/or dolomite absorption.

Relatively elevated 2.15 μm/2.33 μm ratio values are evident for the Mg tholeiite close to shaft 4. Since talc is absent in this lithology and chlorite is less abundant than carbonate minerals, the high ratios are primarily due to the carbonate content of the tholeiite. Since carbonate minerals are not common in unaltered Mg tholeiite, a 600-m carbonate halo is inferred to be present around the ore itself.

The 2.15 μm/1.95 μm ratio shows elevated anomalous values within the mineralized zone. This ratio is considered to reflect the increased amount of adsorbed water in the mineralized zone, which is most likely due to late-stage alteration of minerals formed during the hydrothermal event which formed the deposit. The location of the highest 2.15 μm/1.95 μm ratio values, at the junction between flow ore and green carbonate, lends support to this interpretation.

Whole-rock geochemistry: The three types of ore were found to be geochemically distinct compared with adjacent lithologies, although the flow ore and albitite dike show some similarity, both being enriched in Na and Zr and depleted in Co, Ni, and volatiles (loss on ignition). In addition the flow ore is enriched in Ti, Mn, and Cu, and depleted in K and Ti. The albitite dike ore also shows moderately enhanced levels of Sr and Th. The fuchsite-bearing

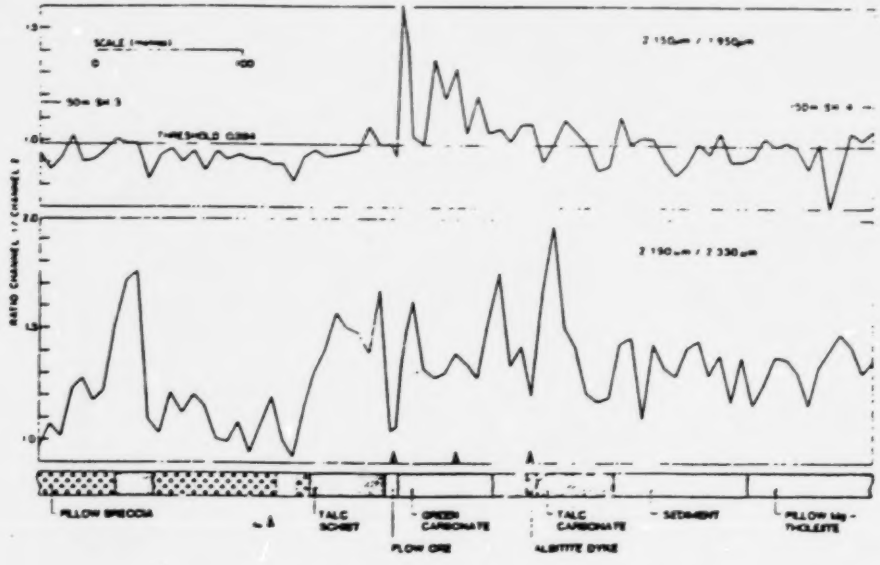

FIG. 8 Radiometer surveys of the Kerr Addison mine (3850 level)

green carbonate is enriched in K, Mg, Co±V±Zn±Ni, and depleted in Al, Ca, and Ti compared to nearby lithologies. The change in carbonate mineralogy from calcite to dolomite toward the ore is reflected by a 200-m zone of erratically high MgO/CaO ratios around the ore itself (Fig. 9).

Northern Ontario gold prospect rock suite

Geology: This gold prospect also lies within the Abitibi orogenic belt. The gold mineralization occurs in a basal, continuous, black cherty quartz zone and in several discontinuous cherty lenses and brecciated quartz zones. Host rocks are rhyodacitic Southern Keewatin volcanics and sediments into which Algoman-age felsic intrusions have been emplaced. The gold mineralized zone occupies a steeply dipping limb of a northwest-plunging fold. The basal chert band is probably exhalative volcanogenic in origin, although the genesis of the mineralized chert lenses is uncertain.

Rock samples were obtained from three drill holes (A, B, and C). Holes A and B pass through pelitic sediments hosting the discontinuous chert lenses, then through the basal ore zone, and finally into chloritic tuff. Samples from core B were only available for mineralized sections. Drill hole C was located approximately 150 m from holes A and B and passes through unmineralized rocks, although the pelitic and psammitic horizon passes laterally into strata bearing the discontinuous chert lenses; the altered feldspar porphyry passes laterally into the basal chert layer.

Light reflectance examination: Examination of the spectra showed that three radiometer filter pairs were suitable to delineate the ore zones: the two filter pairs used above and the clay mineral sensitive (2,100/2,200 nm) pair.

The results of the radiometer survey of the three drill holes are given in Figures 10, 11, and 12. The interpretation of the 2.15/1.95-μ ratio at this prospect is similar to that at Kerr Addison (i.e., it reflects the total adsorbed water content of all minerals present). Since clay minerals were not observed in thin sections of the host rocks, the 2.1/2.2-μ ratio is considered to be sensitive to the degree of sericitic alteration. Sericite is present in both the dacitic and rhyolitic tuff lithologies. Carbonate minerals are mainly present in thin veins throughout the tuff units but may also be present as very fine grains in the tuff groundmass. The 2.15/2.33-μ ratio is most likely to reflect the abundance of carbonate minerals and, dependent on its composition, the distribution of chlorite.

Since SiO_2 (as chert or quartz) exhibits no absorption bands in the visible or near infrared, the chert-hosted gold mineralization is detected by the radiometer as zones of low 2.15/2.33-, 2.15/1.95-, and 2.1/2.2-μ ratio values, indicating the lesser alteration of the siliceous material compared to the altered tuffaceous units. This interpretation is supported by the absence of anomalously low ratios for the discontinuous chert bands in drill hole A, and by the absence of anomalously low 2.15/2.33-μ ratios for the basal chert horizon in drill hole B, which contains many thin carbonate veins.

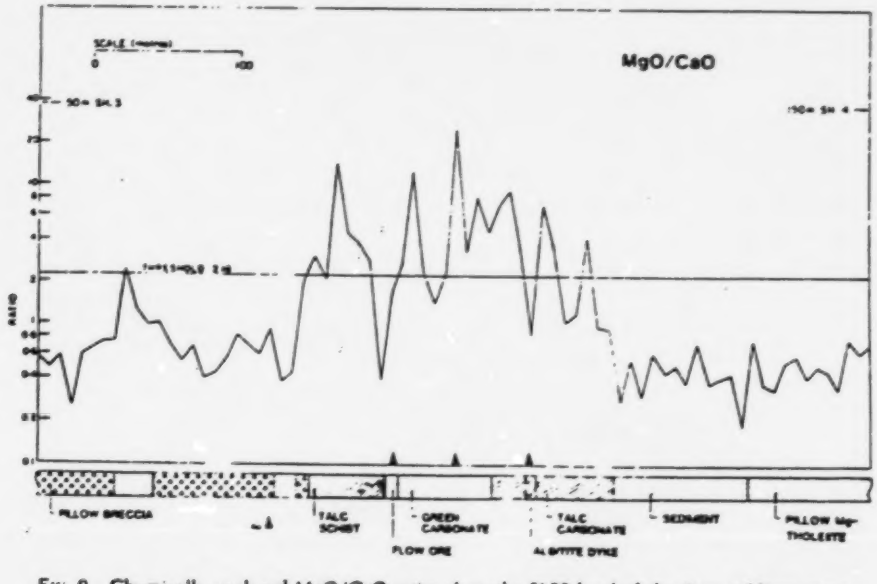

FIG. 9 Chemically analyzed MgO/CaO ratios along the 3450 level of the Kerr Addison mine.

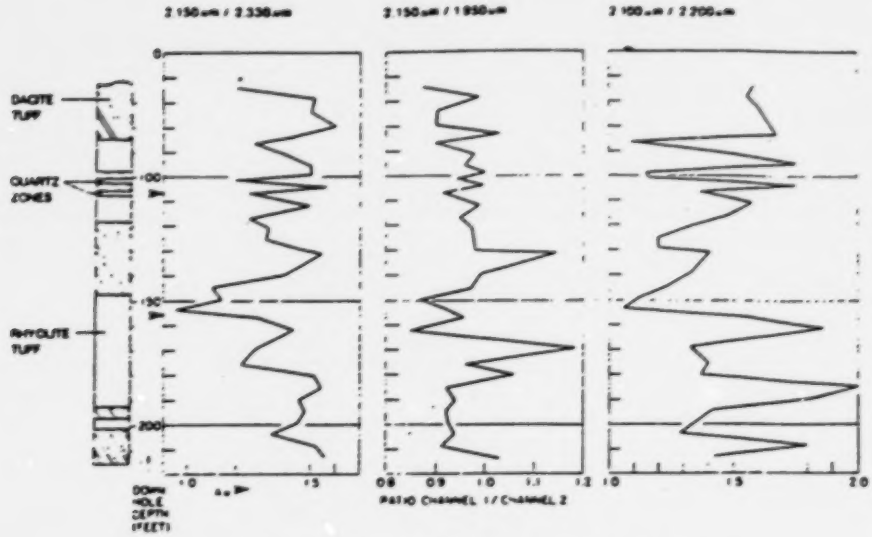

FIG. 10 Radiometer survey of a gold prospect, drill hole A.

In drill hole C all three ratios show high values around the altered feldspar porphyry reflecting the higher adsorbed water (2.15 μm/1.95 μm ratio) and higher sericite (2.1 μm/2.2 μm ratio) contents of the altered rocks. Since carbonate minerals are not abundant around the altered feldspar porphyry, the elevated 2.1 μm/2.33 μm ratios are thought to be caused by the increased chlorite content of the intrusive relative to the rocks above it, and also to the high chlorite content of the tuff below the feldspar porphyry.

Whole-rock geochemistry: The upper, gold-bearing chert lenses were found to be geochemically distinct from the basal ore zone. The discontinuous lenses are enriched in Ag ± Mo ± Cu ± Pb and depleted in Al_2O_3, K_2O, FeO, TiO_2, MnO, CaO, MgO, Be, Co, Zr, Zn, V, and Sr compared to the basal ore zone. The basal ore zone shows outstanding enrichment in Al_2O_3, K_2O, P_2O_5, Th, Sr, Mo ± Sr ± Be and depletion in Fe_2O_3, CaO, MgO, TiO_2, MnO, Co, V, Zn ± Ni with respect to the adjacent lithologies.

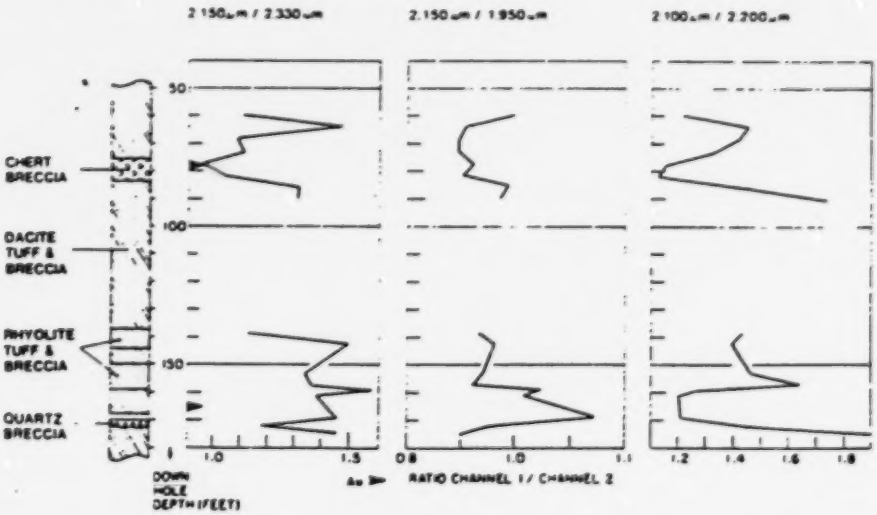

FIG. 11. Radiometer survey of a gold prospect, drill hole B.

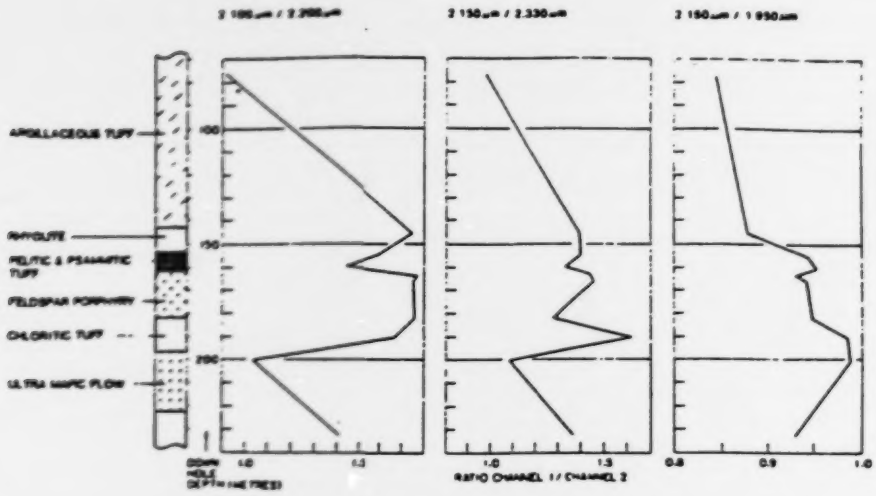

FIG. 12. Radiometer survey of a gold prospect, drill hole C.

Precision of radiometer ratio measurements: Sixty blind, duplicate measurements of the three ratios were distributed through the radiometer monitoring of the rock samples. The samples were reorientated for duplicate measurements, with in most cases a time lapse of >2 h between replicate determinations. The precision for all three ratios at the 95 percent confidence level was 10 percent.

Since the precision of replicate radiometer determinations on a target has been shown to be less than 0.5 percent (see above discussion), most of the observed error for replicate sample determinations must be due to sample inhomogeneity. This fact suggests that sample pulverization prior to ratio measurement would improve batch precision. However, if comparison between radiometer ratio results and multielement geochemical data is to be carried out, the precision achieved during the above batch measurements is considered to be suitable.

Discussion

Although laboratory analysis of solar reflectance spectra has been used extensively in remote sensing to detect geologic variations and hydrothermal alteration patterns, field confirmation of mineralogic changes using portable reflectance radiometers is a relatively new approach. Consequently careful examination of the operating parameters of such instruments prior to field use is essential; in particular it is necessary to establish sources of error during routine measurements. Detailed examination of the Barringer hand-held reflectance radiometer under controlled laboratory conditions has established that this instrument may be operated continuously for up to 16 h with only a 4 percent signal change and that maximum observed signal error at the 99 percent confidence level is only 0.5 percent.

Moreover, the ratio of reflected light at two wavelengths in the infrared range is unchanged by incident light intensity and by target geometry, although ratio variations do occur with different target textures. The field of view of the radiometer is 28 × 4 cm and as such is relatively large for examination of small geologic specimens. A small optical device attached to the instrument will reduce the field of view to 8 × 1 cm. Using this attachment measurements can be made on materials such as diamond drill core.

The radiometer's optical filter selection has been made from reflectance spectra for common rock-forming minerals generated by the Barringer scanning reflectance spectrometer. Calibration studies have demonstrated a linear relationship between reflectance ratios measured using the radiometer with several filter combinations and varying quantities of common alteration minerals such as chlorite, kaolinite, and montmorillonite. This shows that the instrument may be employed for semiquantitative estimation of specific mineral content in a rock given known petrological constraints. It is important to note, however, that the authors have not indicated the feasibility, using the radiometer, of rapid mineralogic analyses on any natural mineral assemblage. A general knowledge of likely mineralogic changes is requisite for confident interpretation of reflectance data.

Measurements made with the radiometer on suites of geologic hand specimens from the Kerr Addison

gold mine and a gold prospect in Ontario emphasize that reflectance spectrometry can rapidly and precisely monitor variations in hydrothermally altered drill core and rock samples.

Although portable radiometers may be used to delineate carbonate and clay mineral alteration halos which may be visible in hand specimens, they serve an additional function in detecting more subtle guides to hydrothermal alteration (e.g., adsorbed water content).

Geochemical analysis of rock samples from the Kerr Addison gold mine revealed anomalous MgO/CaO values over the mineralization. Clearly, the ability to discriminate between carbonate minerals by reflectance spectrometry would be a considerable aid to mineral exploration in geologic terrain exemplified by the Abitibi belt. Similarly, the ability to discriminate between and provide rapid semiquantitative analyses of individual clay minerals would be of advantage in exploration for other types of mineralization (e.g., base metals, uranium, petroleum). Current research by the authors is being directed toward this aim.

Although this work has concentrated on monitoring of drill core and rock samples, it is anticipated that the methods used are directly applicable to monitoring other sample media such as basal till and stream sediment. Where large numbers of such samples are submitted for geochemical analysis, initial screening by reflectance spectrometry may prove to be economically advantageous.

Conclusions

The Barringer hand-held reflectance radiometer has suitable operating characteristics for routine, field mineral exploration. It may also be used with confidence in the laboratory to provide instant, precise, and low-detection limit semiquantitative estimates of a selection of diagnostic alteration minerals. This radiometer has been shown to be capable of distinguishing alteration halos around hydrothermal gold mineralization in northern Ontario in both hand specimen and drill core rock samples. Such information is invaluable in routine exploration for gold mineralization. It is anticipated that the methods used are readily applicable to exploration for other types of mineralization.

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REFERENCES

Collins, W., and Chang, S. H., 1982, Summary of new airborne remote sensing techniques developed for mineral and oil exploration and geologic mapping: Unpub Rept., Aldridge Lab Appl Geophysics, Columbia Univ., 65 p.

Davies, J., Dick, R., and Cumming, C., 1981, A field reflectance spectrometer: Canadian Symposium Remote Sensing, 7th, Winnipeg 1981, Proc., p. 416–422.

Daubner, L., Davies, J., and Goetz, A., 1981, A hand-held ratioing radiometer for remote radiance measurements: Canadian Symposium Remote Sensing, 7th, Winnipeg 1981, Proc., p. 423–428.

Goetz, A. F. H., Rowan, L. C., and Kingston, J., 1982, Shuttle multispectral infrared radiometer: Preliminary results from the second flight of Columbia, *in* Internat. Geoscience Remote Sensing Symposium, Munich 1982, Proc.: New York, Inst. Electrical Electronics Engineers, v. 2, p. FA 6.3–6.5.

Hunt, G. R., and Ashley, R. P., 1979, Spectra of altered rocks in the visible and near infrared: Econ. Geol., v. 74, p. 1613–1629.

Hunt, G. R., and Salisbury, J. W., 1970, Visible and near-infrared spectra of minerals and rocks: I. Silicate materials: Modern Geology, v. 1, p. 283–300.

—— 1971, Visible and near-infrared spectra of minerals and rocks: II. Carbonates: Modern Geology, v. 2, p. 23–30.

Hunt, G. R., Salisbury, J. W., and Lenhoff, C. J., 1971, Visible and near-infrared spectra of minerals and rocks: III. Oxides and hydroxides: Modern Geology, v. 2, p. 195–205.

—— 1973a, Visible and near-infrared spectra of minerals and rocks: VI. Additional silicates: Modern Geology, v. 4, p. 217–224.

—— 1973b, Visible and near-infrared spectra of minerals and rocks: VII. Acidic igneous rocks: Modern Geology, v. 4, p. 217–224.

—— 1973c, Visible and near-infrared spectra of minerals and rocks: VIII. Intermediate igneous rocks: Modern Geology, v. 4, p. 273–344.

—— 1974, Visible and near-infrared spectra of minerals and rocks: IX. Basic and ultrabasic igneous rocks: Modern Geology, v. 5, p. 15–22.

Rowan, L. C., and Kahle, A. B., 1982, Evaluation of 0.46- to 2.36-μm multispectral scanner images of the East Tintic mining district, Utah, for mapping hydrothermally altered rocks: Econ. Geol., v. 77, p. 441–452.

Sadowski, R., and Abrams, M., in press, Mapping hydrothermal alteration using aircraft VNIR scanners at the Rosemont copper deposit: Internat. Symposium Remote Sensing Environment, 2nd, Ft. Worth 1982, Proc.

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THE APPLICATION OF RAPID, SEMI-QUANTITATIVE CLAY MINERAL DETERMINATION AT THE CORTEZ GOLD MINE, NEVADA

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measured using a simple scanning spectrometer with a standard Barringer Hand Held Ratioing Radiometer (HHRR) incorporated as the detector. HHRR is designed to measure reflected light energy from a target in two narrow passbands, selectable in the range 400 to 2800 nm. The selectable instrument output (liquid crystal digital display and analogue output) provides; (1) the power through each passband (channel);(2) the ratio of the two channel outputs (channel 1/channel 2).

Instrument design is shown schematically in Figure 2. The instrument has an optical train for each channel. After passing through a chopper, which modulates the incoming DC reflected energy for both channels, the light is focussed onto, and a portion passes through, an operator selectable filter, after which the light is refocussed onto a thermoelectrically cooled PbS detector. HHRR design is fully discussed by Daubner et al (1981).

The HHRR was rigidly mounted perpendicular to the exit slit of a Jarrell Ash (Model 82-40) 0.25 metre monochromator. A tungsten filament, quartz envelope light source was mounted at the inlet slit. The mounting allows adjustment of light source position in three dimensions to allow:

a) focussing of the filament image on the inlet slit using a concave, front aluminium coated mirror with focal length of 10 cm;
b) optimum illumination of the diffraction grating and monochromator mirrors.

The lamp current is stabilized and lamp voltage is continuously monitored. An external chopper was mounted close to the monochromator inlet slit and the phase reference signal was supplied to the HHRR. The HHRR's internal chopper was disabled during measurement and all optical filters removed.

The internal mechanism of the monochromator was altered to allow:

a) a scan from 450 nm to 1.0 micron using a 600 blaze grating and one order sorting filter at 590 nm (HHRR acts as the order sorting filter for wavelengths less than 300 nm);
b) a scan from 1.0 to 2.82 microns using a 300 blaze grating and order sorting filters at 1.0 and 1.6 microns.

The PbS detectors in HHRR are insensitive to wavelengths beyond 3.2 micrometers. The monochromator slit width during measurement was 2.57 mm which corresponds to a half-peak band pass of approximately 25 nm in the 1.0 to 2.8 micron region.

Channel 2 of the HHRR continuously monitors a reference beam, deflected from the exit beam using a front coated plane mirror. Channel 1 of the HHRR continuously monitors sample reflectance at an angle of 30° from normal.

Measurement Technique

Samples for reflectance measurement were hand ground to minus 40 mesh, plus 200 mesh. Hand grinding is not necessary for reflectance measurements using a standard HHRR. However, the field of view of the HHRR spectrometer is only 2 x 0.5 cm. and hand grinding is necessary in order to obtain a homogenous sample on which reflectance may conveniently be measured. The purpose of using the HHRR-spectrometer was to obviate the purchase of a large number of optical filters during research.

The hand ground sample is placed into a cardboard tray to a depth of approximately 2 mm. The tray allows accurate positioning of the sample in the instrument field of view with a reproducible HHRR-sample viewing distance. Repeat measurements of a number of samples including refilling of the tray and re-measurement of sample reflectance showed that the measurement error in the 1.0 to 2.8 micrometer wavelength region varied between 0.5 and 5 percent of the reflectance value.

Ambient Humidity

In order to quantify the effect of changing ambient humidity on reflectance measurements the HHRR-spectrometer described above was placed in a large, sealed plexiglass glove box and the interior humidity was controlled using appropriate saturated solutions (eg. a saturated solution of lithium chloride will maintain a constant humidity of 15 percent in a closed atmosphere; other saturated solutions will maintain different levels). The interior humidity was homogenized using a circulation fan, the absolute humidity was monitored using a Lyman Alpha detector, and the internal temperature was monitored. The experimental procedure consisted of placing a sample tray and a barium sulphate reflectance standard inside the glove box with the HHRR-spectrometer and the appropriate saturated solution. The fan was switched on and the closed system was left overnight to equilibrate. Following equilibration sample reflectance was measured at 1.86, 1.9, 2.1, 2.2, 2.65, 2.71, 2.73 and 2.75 micrometers. The results obtained at three ambient humidities ranging from 15 to 66 percent for kaolinite, smectite, muscovite, illite and chlorite are presented in Table 1 and indicate that the observed changes in reflectance are similar in magnitude to the measurement error.

Calibration Clay Minerals

Reflectance measurements of each batch (10-15) of samples was accompanied by similar measurements on calibration minerals including kaolinite, smectite, illite, muscovite, chlorite and biotite. Where possible recognized standard mineral specimens were obtained and each specimen was checked for purity by the x-ray diffraction laboratory at the Geological Survey of Canada. Details of the calibration minerals used are given in Table 2.

DEVELOPMENT OF A SPECTRAL DECONVOLUTION ALGORITHM

The development of a spectral deconvolution algorithm was carried out empirically. The reflectance of interfering minerals together

with the calibration minerals and samples containing known (XRD) contents of alteration minerals were measured at a large number of wavelengths in the 1.8 to 2.8 micrometer wavelength region. The optimum wavelengths for deconvolution were then selected such that interference from other minerals was minimized. Various algorithms were tested to determine their effectiveness at semi-quantitatively estimating the calibration mineral content of the samples.

Spectra of Interfering Minerals

Reflectance measurements were obtained on specimens of biotite, hornblende, augite, alunite, gypsum, talc, pyrophyllite and an illite/smectite mixed layer clay. The reflectance data for selected wavelengths are presented in Table 3. The spectrum of biotite is very similar to that of kaolinite in the 2.65 - 2.8 micrometer region and, due to its natural abundance, was included in the minerals which required determination. Hornblende, augite, talc and pyrophyllite also show absorption in the 2.65 - 2.8 micrometer region. However, since they are in general less common than the minerals to be determined, it was decided to allow their selective inclusion in any subsequently developed algorithm by substitution with a mineral not considered to be present. Alunite and gypsum do not show marked absorption in the 2.7 micrometer region although both show a shoulder at 1.9 micrometers and an absorption feature close to 2.17 micrometers. The technique for dealing with the presence of either alunite or gypsum is discussed below.

Using a mixture of empirical results and correlation analysis, the optimum wavelengths for spectral deconvolution were found to be 1.86, 1.90, 2.65, 2.68, 2.71, 2.73, 2.75 and 2.77 micrometers. The 1.86, 2.65 and 2.68 micrometer wavelengths are reference wavelengths which are used to determine the relative depth of the clay mineral sensitive absorption features. The 1.90 micrometer wavelength is used to distinguish the very similar spectra of smectite and smectite/illite mixed layer clays from illite which only shows a shallow 1.90 micrometer reflectance feature.

Spectal Deconvolution Algorithm

Gladwell (1982) demonstrated that the functions relating modal percent mineral and HHRR ratio response were approximately linear in the 2.65 - 2.8 micrometer region where overcoating of the one mineral on another was not allowed to occur (Figure 3). This suggested that the overlapped absorption features of different minerals are approximately a linear combination of the individual feature producing minerals. However, the use of a simultaneous equation algorithm by this worker was not particularly successful primarily because:

a) the sample background spectra (sample with all clay minerals removed) were more complex than was anticipated;
b) small measurement errors propagate using simultaneous equations producing large errors in the final result.

Following this failure three other types of algorithm were attempted:

a) correlation analysis;
b) stepwise multiple regression;
c) least squares fit with empirical selection rules.

The closest agreement between XRD and reflectance results was obtained using an algorithm incorporating the least squares fit criteria and a series of empirical selection rules.

This deconvolution algorithm is relatively simple and consists of three steps which are discussed below. The algorithm flow diagram is presented in Figure 4.

STEP 1: For all combinations of pairs of mineral standards a mixed spectrum is mathematically produced that closely matches the sample (unknown) spectrum.

STEP 2: From this spectral set, the best fitting spectra (minimum of five) are selected and a weighted average (weighted by the sum of squared deviations) of the amounts of minerals used to form these spectra is calculated as a first estimate of the sample mineral contents.

STEP 3: The first, weighted average, estimate is then adjusted using a set of empirically derived selection rules developed to minimize errors due to known spectral interferences. The selection rules are used to decide whether smectite, illite, muscovite or a mixed layer illite/smectite is present with either kaolinite/biotite and/or chlorite.

Estimation of Spectral Background

The algorithm accepts a value in volts from the HHRR (calibrated using a barium sulphate reference panel) for each of the wavelengths listed above. The clay mineral sensitive wavelengths are ratioed to the reference wavelengths to give six reflectance ratios: 1.9/1.86; 2.65/2.68; 2.65/2.71; 2.65/2.73; 2.65/2.75; 2.65/2.77. An inferred spectral baseline is then calculated from these ratios and the actual sample ratios together with the inferred baseline ratios are input to the algorithm. The method of inferring the baseline ratios is depicted in Figure 5 for the case where gypsum or alunite are not considered to be present. The 1.9/1.86 baseline ratio is assumed to equal zero. The baseline ratios for the 2.71-2.77 micrometer region are calculated by projecting a baseline through the 2.65/2.65 ratio (equal to unity) and the 2.65/2.68 ratio for the 2.65/2.71, 2.65/2.73 and the 2.65/2.75 baseline ratios. The 2.65/2.77 baseline ratio is set equal to the 2.65/2.75 baseline ratio (See dotted line in Figure 5).

Where alunite or gypsum may also be present in the unknown sample the 1.86 micrometer reference value is accompanied by a

measurement at 2.0 micrometers. The mean of the 1.86 and 2.0 micrometer values is then ratioed to the 1.9 micrometer ratio to give the sample ratio corrected for the presence of alunite or gypsum. This procedure is used because the presence of alunite and gypsum cause a marked decrease in reflectance from 1.86 towards the 2.17 absorption feature which would indicate the presence of smectite if not corrected for.

LABORATORY RESULTS

XRD and HHRR determined contents are compared in Figures 6 and 7 for smectite/illite, smectite, mixed layer clays and kaolinite/biotite respectively for the test suite of 53 samples. The test suite results showed that where a mineral was present in quantity greater than 10 percent (as determined by XRD) the algorithm correctly determined the mineral group (defined as: (1) kaolin/biotite; (2) smectite, muscovite and illite; (3)chorite) in 94 percent of cases. The mean error in estimating mineral quantity was less than 13 percent absolute. In determining individual minerals, the algorithm correctly classified 67 percent of the samples with an error of less than 20 percent absolute in quantification. Eighty two percent of the erroneous classifications were associated with classification of muscovite, illite and smectite. The most common misclassifications were in identifying illite as muscovite and a mixture of smectite and illite as smectite.

Although pure samples of kaolinite and biotite are distinguishable in the 2.7 micrometer region, the test results showed that in natural samples they were not easily distinguished. Therefore, the algorithm outputs the estimated mean of kaolinite and biotite contents as kaolinite/biotite.

Errors may be assigned as follows:

1. Error will occur if the calibration mineral spectra are dissimilar to those of the minerals actually present in the sample. This is most likely to be a problem with smectite and illite, partly due to the difficulty in obtaining pure, characterized samples.
2. Measurement errors. Experience has shown measurement errors in data collection are less than 4%.
3. XRD analytical errors. XRD is not designed primarily as a quantitative method and the analytical errors are at least ± 10%, particularly where more than two minerals are present in the sample. However, XRD mis- classification errors are unlikely.
4. The HHRR technique determines modal (by area) mineral content whereas the XRD technique determines bulk (weight %) content. The two determinations are not compatible in all cases, particularly where overgrowing of minerals occurs.
5. Changes in ambient humidity. Our work has shown that provided a $BaSO_4$ reflectance target is used; changes in ambient humidity in the range 1% to 66% relative humidity change the reflectance spectra by less than the measurement error.
6. Errors in estimating the background spectrum (the spectrum of the sample with all clays removed) of the sample. This source of error is difficult to quantify and must be the subject of further research.

HORSE CANYON FIELD SURVEY

Geology of the Horse Canyon Area

The Horse Canyon epigenetic gold deposit is located approximately 5 km. southeast of the Cortez Gold Mine, Nevada (Figure 8). The major structural features of the Cortez area are the range front fault (Crescent Valley Fault) and the Roberts Mountain Thrust (RMT). The Horse Canyon deposit lies on a postulated extension of the RMT.

The rocks of the lower plate of the RMT include the Hamburg Dolomite (Cambrian), Eureka Quartzite and Hanson Creek Formation (Ordovician), Roberts Mountain Limestone (Silurian), Wenban Limestone (Devonian) and the Pilot Shale which is also Devonian in age. Except for the Eureka Quartzite all the formations are dominantly carbonate facies.

The rocks of the upper plate of the RMT include the Valmi and Vinini Formations (Ordovician), the Elder Sandstone and Fourmile Canyon Formation (Silurian) and the Slaven Chert (Devonian). The upper plate rocks are dominantly siliceous in composition.

In the Horse Canyon area only the Wenban Limestone (Dw) of the lower plate and the Vinini Formation (Ov) of the upper plate rocks are represented (Figure 9). The following descriptions of these two lithologies are extracted from Silluly and Masursky (1965) and Wells et al (1969).

At Cortez the Wenban Limestone has a gradational boundary with the underlying Roberts Mountain Limestone although elsewhere (Carlin) the two formations are unconformable. The Wenban Limestone consists of approximately 600 meters of interbedded dark-grey, thick-bedded bioclastic and thin-bedded grey to yellow grey, argillaceous, slabby limestones. The limestone becomes lighter grey, finer grained and more massive up through the section.

In the type locality (Vinini Creek) the Vinini Formation consists of quartzite, psammitic limestone and siltstone, chert, clay, shale, organic rich shale and some andesitic volcanic rocks. In the area examined, how- ever, the Vinini is represented by fine grained psammites and psammitic shales.

A rock sampling traverse was carried out across the thrust zone above the main ore body. Sample locations are presented in Figure 9 which also shows the principal faults within the thrust zone. Three additional samples (not shown in Figure 9)

were collected along the main haulage road in order to estimate background reflectance values of the Wenban Limestone.

Around and within the ore zone there is local development of jasperoid bodies - although they do not appear to be directly related to either the faults or the ore disposition.

Samples were submitted for geochemical analysis and their reflectance was measured at the wavelengths necessary for semi-quantitative clay mineral determination. In addition, five of the rock samples were submitted for semi-quantitative XRD mineralogical analysis.

HORSE CANYON FIELD SURVEY RESULTS

The reflectance data are given in Table 4, the clay mineral analysis in Table 5 and selected geochemical results in Table 6.

Variation of the 2.65/2.75 reflectance ratio across the thrust zone in the Horse Canyon area is shown in Figure 10 together with the aluminium and potassium oxide content. The rock geochemistry was determined by sample dissolution using an $HF-HNO_3-HClO_4$ acid mixture followed by introduction into an inductively coupled argon plasma emission spectrometer.

High reflectance ratios and increased abundance of potassium and aluminium oxides occurs over fault zones and suggests the development of clay alteration associated with these faults. The high correlation ($R = +0.92$) between the 2.65/2.75 reflectance ratio and the aluminium oxide content of the samples clearly demonstrates the effect of the presence of illite (in this case) on the sample reflectance. The fault zones picked out by the reflectance data show high Be, Cu, Ba, Sr and Zr values although the Ba and Sr values are also elevated in the Wenban limestone samples (Table 6).

The abundance of illite/muscovite and kaolinite determined by deconvolution of the reflectance data, presented in Figure 11, shows the marked increase in clay mineral content in the thrust zone compared with background samples collected along the main haulage road. There is a marked increase in muscovite/illite over the ore zone and a slight increase of kaolinite/ biotite within the thrust zone but outside the ore zone. There is no obvious relationship between the distribution of clay minerals and the jasperoid bodies, although the jasperoid bodies are clearly defined by the total geochemical Fe content of the rock samples.

The available XRD data (Table 7) agrees with the reflectance algorithm in selecting illite as the primary clay mineral present. Only minor amounts of kaolinite were detected by XRD although the reflectance algorithm indicates a larger amount was present.

DEVELOPMENT OF A FIELD PORTABLE CLAY MINERAL ANALYSIS SYSTEM: 'CLAYPAK'

Consequent on the success of the laboratory tests, the agreement between XRD and reflectance determined clay mineral contents of the test sample suite and the demonstrated usefulness of the technique in the Horse Canyon field area, a field portable reflectance system of clay mineral analysis was developed. The developed system, called CLAYPAK, is shown in Figure 12. CLAYPAK incorporates a standard Barringer Hand Held Reflectance Radiometer Mk II which is mounted on a tripod. Radiance data (in volts) obtained by the HHRR are transmitted to an EPSON HX-20 microcomputer via a twisted pair shielded cable. The EPSON microcomputer and the HHRR operate off the same 6 volt, 7.5 ampere hour gel cell battery which is conveniently mounted on an operator worn belt. Power to the microcomputer is regulated inside the Epson HX-20 unit where digitization of HHRR data also occurs. The clay mineral deconvolution algorithm together with data logging software is stored on micro-cassette. The software itself is coded in assembly language and Epson basic. Only those portions of the software for which high operating speed is required are coded in assembly language (eg. the empirical selection rules are coded in Epson basic to allow operator modification). The approximately 500,000 arithmetic operations required for a single clay mineral analysis are computed using a floating point arithmetic processing unit which requires approximately 10 seconds to perform a single clay mineral analysis. Following radiance measurements using the HHRR, algorithm processing, storage of the raw data, field notes and clay mineral contents are accomplished by the microcomputer in approximately 30 seconds. The arithmetic processing unit and associated hardware are packaged in a standard Epson expansion interface module, the extra RAM remaining accessible to the operator. Finally, the system also includes a Lowell Omni tungsten iodide, quartz envelope light source (optional 12 V DC or 117 V AC power supply) and a standard HHRR core viewing attachment (C.V.A.). The field of view of the C.V.A. is approximately 5 cm. x 1.5 cm with a focal length of approximately 30 cm.

The scenario envisaged for operation of the CLAYPAK system is a field camp or drill core storage shack where power for the light source is available. Samples obtained during field work would then be brought to the field unit for analysis. Alternatively, the CLAYPAK unit could operate in a true roaming mode, although suitable batteries supplying power to the light source would have to be carried by the operator in a backpack.

CONCLUSIONS

1. A rapid and cost-effective semi-quantitative field technique for analysis of kaolinite, smectite, smectite/illite mixed layer clay minerals, illite, muscovite and chlorite has been developed and tested. Good agreement with XRD semi-quantitative mineralogical analysis has been demonstrated. Suitable,

field portable instrumentation is now available for clay mineral analysis. The instrumentation enables rapid semi-quantitative estimation of clay mineral assemblages, is applicable to mapping alteration patterns over both base and precious metal prospects and to defining clay mineral alteration haloes in drill core and for remote sensing groundtruthing purposes.

2. At Horse Canyon, Nevada, variation of the 2.65/2.75 reflectance ratio and aluminium and potassium oxide content show a high correlation over the thrust zone and demonstrates a close relationship between faulting and clay mineral alteration.
3. At Horse Canyon, clay mineral abundances determined by the deconvolution algorithm indicates that illite/muscovite is the most prominent clay mineral within the area of the gold ore body, in agreement with X-ray diffraction results.

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REFERENCES

1. Collins, W. and Chang, S.H., 1982, "Summary of New Airborne Remote Sensing Techniques Developed for Mineral and Oil Exploration and Geologic Mapping", Unpub. Rept., Aldridge Lab. Appl. Geophys, Columbia Univ., 65 p.
2. Daubner, L.R., Davies. J.H., and Geotz. A., 1981. "A Hand Held Ratioing Radiometer for Remote Radiance Measurements", Canadian Symposium Remote Sensing, 7th, Winnipeg 1981, Proc., p. 423-428.
3. Gladwell, D.R., 1982, "Application of Reflectance Spectrometry to Clay Mineral Determination in Geological Materials Using Portable Radiometers", International Symposium Remote Sensing Environment, 2nd., Fort Worth 1982, Proc. Vol. 1, p. 29-38
4. Gladwell, D.R., Lett, R.E., and Lawrence, P., 1983 "Application of Reflectance Spectrometry to Mineral Exploration Using Portable Radiometers", Economic Geology, Vol. 78, p. 699-710.
5. Gilluly, J. and Masursky, H. 1965, "Geology of the Cortez Quadrangle Nevada", U.S. Geol. Surv. Bull. 1175, 117 p.
6. Hunt, G.R. and Ashley, R.P. 1979, "Spectra of Altered Rocks in the Visible and Near Infrared", Economic Geology, v. 74, p. 1616-1629.
7. Hunt, G.R. and Salisbury, J.W., 1970, "Visible and Near Infrared Spectra of Minerals and Rocks", I. Silicate Materials: Modern Geology, v. 1, p. 283-300.
8. ----- 1971, "Visible and Near Infrared Spectra of Minerals and Rocks", II. Carbonates: Modern Geology, v. 2, p. 23-30.
9. Hunt, G.R., Salisbury, J.W. and Lenhoff, C.J., 1971, "Visible and Near-Infrared Spectra of Minerals and Rocks", III. Oxides and Hydroxides: Modern Geology, v. 2, p. 195-205.
10. ----- 1973a. "Visible and Near-Infrared Spectra of Minerals and Rocks", VI. Additional silicates: Modern Geology, v. p. 217-224.
11. ----- 1973b. "Visible and Near-Infrared Spectra of Minerals and rocks", VII. Acidic Igneous Rocks: Modern Geology, v. 4, p. 217-224.
12. ----- 1973C. "Visible and Near-Infrared Spectra of Minerals and Rocks: VIII. Intermediate Igneous Rocks", Modern Geology, v. 4, p. 273-344.
13. ----- 1974. "Visible and Near-Infrared Spectra of Minerals and Rocks: IX. Basic and Ultrabasic Igneous Rocks", Modern Geology, v. 5, p. 15-22.
14. Huntington, J.F., 1984. "Interpretation of Visible, Near and Short Wavelength Infrared, Field and Airborne Spectra from Mary Kathleen, Queensland, Australia", International Symposium Remote Sensing Environment, 3rd., Colorado Springs 1984, Summaries, p. 31.
15. Rowan, L.C. and Kahle, A.B., 1982, "Evaluation of 0.46 to 2.36 um Multispectral Scanner Images of the East Tintic Mining District, Utah, for mapping hydrothermally altered rocks", Economic Geology v. 77, p. 441-452.
16. Sadowski, R.M. and Abrams, M.J., 1982. "Mapping Hydrothermal Alteration Using Aircraft VNIR Scanners at the Rosemont Porphyry Copper Deposit", International Symposium Remote Sensing Environment, 2nd., Fort Worth 1982, Proc. vol. 1, p. 175-188.
17. Segal, D.B., Ruth, M.C., Merin, I.S., Watanabe, M., Soda, K., Takano, O., and Sano, M., 1984. "Spectral Remote Sensing Investigation of Lisbon Valley, Utah", International Symposium Remote Sensing Environment, 3rd., Colorado Springs 1984, Summaries, p. 37-39.
18. Van der Marel, H.W. and Beutelspacher, H., 1976. "Atlas of Infrared Spectroscopy of Clay Minerals and Their Admixtures". Elsevier, Amsterdam, Oxford, New York, 396 p.
19. Wells, D.W., Stoiser, L.R. and Elliott, J.E., 1969, "Geology and Geochemistry of the Cortez Gold Deposit, Nevada", Economic Geology, vol. 64, p. 526-537.

TABLE 1:

Reflectance of Pure Minerals Relative to $BaSO_4$ at:
(A) 15%; (B) 52%; (C) 66% Relative Humidity

Wave-Length (Micro-meters)	Kaolinite			Smectite			Muscovite			Illite			Chlorite		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
1.86	80	79	79	85	86	88	66	66	68	49	50	51	46	46	47
1.9	80	79	78	69	68	69	67	66	68	46	46	47	48	48	50
2.1	73	72	72	82	83	83	66	66	68	53	53	54	56	55	57
2.2	53	51	51	76	77	78	60	59	61	47	46	47	58	57	59
2.65	42	40	40	57	56	57	61	61	63	39	37	38	58	57	59
2.71	21	18	19	38	36	38	53	52	54	26	24	24	56	55	56
2.73	19	17	17	29	26	28	40	38	40	20	18	19	53	50	51
2.75	23	19	21	26	23	23	29	26	27	20	16	17	41	40	40

TABLE 2: Details of Calibration Minerals Selected for Comparison With Test Sample Suite.
(selected from several specimens of each mineral).

MINERAL	ACCESS CODE	SOURCE/COMMENTS
KAOLINITE	KGA-1	Source Clay Minerals Repository, University of Missouri (Washington County, Georgia). Characterized by XRD* as pure, well crystallized kaolin with no dickite present.
SMECTITE	STX-1	Source Clay Minerals Repository (Gonzales County, Texas). Characterized by XRD* as pure montmorillonite with a 15 angstrom dry and 17.6 angstrom glycolated D spacing.
MUSCOVITE	Mu-W-3	Wards Characterized by XRD* as illite with very good peak resolution. Contains trace quartz.
ILLITE	I-W-2	Wards. (Illinois). Characterized by XRD* as illite with quartz and minor kaolin.
CHLORITE	C-W-4	Wards. Characterized by XRD* as an impure, Fe-rich chlorite. Several small unidentified XRD peaks.
BIOTITE	B-W-13	Wards. (Not analyzed by XRD).
ILLITE/ SMECTITE	ISMt-1	Source Clay Minerals Repository. Characterized by XRD as a mixed chlorite-smectite with quartz and plagioclase

* X-Ray Diffraction analysis performed by the Geological Survey of Canada.

TABLE 3: Reflectance Relative to $BaSO_4$ of Interfering Minerals

Wave-Length (Micro-meters)	Biotite	Horn-blende	Augite	Alunite	Gypsum	Talc	Pyrophy-llite	Illite/ Smectite
2.1	80	75	49	55	67	93	78	57
2.2	81	75	50	41	57	93	60	48
2.65	81	75	61	44	36	94	49	34
2.71	50	49	57	41	31	88	31	25
2.73	47	43	47	40	30	65	27	22
2.75	56	50	43	37	29	61	29	21
2.77	64	63	45	35	29	91	34	25

TABLE 4: Horse Canyon, Reflectance Ratios.

	Reflectance Ratio (wavelengths in micrometers).				
Sample	1.9/1.86	2.65/2.71	2.65/2.73	2.65/2.75	2.65/2.77
52	.975	.967	.931	.878	.836
27	.967	.967	.951	.902	.850
29A	.988	1.233	1.436	1.582	1.574
29B	.979	1.174	1.328	1.444	1.518
31	.966	1.181	1.270	1.294	1.317
32	.956	1.028	1.065	1.159	1.185
33	.970	.967	.965	.992	1.008
34	.968	1.053	1.106	1.227	1.291
35	.988	1.282	1.503	1.573	1.575
36	.970	1.043	1.066	1.081	1.116
37	.976	1.213	1.383	1.490	1.572
38	.985	1.065	1.148	1.274	1.364
39	.984	1.038	1.093	1.180	1.224
40	.965	1.018	1.053	1.096	1.102
41	.974	1.095	1.224	1.453	1.534
42	.981	1.003	1.032	1.138	1.160
43	.978	1.111	1.209	1.334	1.379
44	.972	1.124	1.209	1.306	1.335
45	.972	1.025	1.058	1.142	1.195
46	.964	1.121	1.305	1.525	1.765
47	.975	1.111	1.245	1.427	1.520
48	.982	1.092	1.163	1.200	1.201
50	.976	1.329	1.518	1.581	1.572
51	.982	1.099	1.171	1.250	1.310
*24	.971	.968	.942	.900	.841
*25	.968	.965	.950	.905	.849
*26	.965	.966	.947	.898	.838

* Samples of Wenban Limestone from the haulage road.

TABLE 5: Horse Canyon, Reflectance determined Clay Mineral Content

Sample	Clay Mineral Analysis (Modal %)* Kaolinite/Biotite	Illite/Muscovite	Chlorite
52	0	0	0
27	0	0	0
29A	10	20	1
29B	0	7	1
31	16	19	1
32	20	2	9
33	0	0	0
34	9	3	6
35	16	20	0
36	11	7	1
37	19	26	1
38	1	13	0
39	5	18	1
40	13	25	1
41	2	18	1
42	6	15	0
43	3	3	1
44	8	11	1
45	8	14	1
46	8	46	8
47	6	22	0
48	3	6	0
50	22	17	1
51	7	15	0
-24	0	0	0
-25	0	0	0
-26	0	0	0

* Smectite or Smectite/Illite mixed layer clay minerals were not detected

- Samples of Wenban Limestone from the haulage road.

TABLE 6: Horse Canyon Traverse Selected Geochemical Results. (Samples 29A,B, 35, 41 Collected Near Faults).

Sample	Al_2O_3 %	Fe_2O_3 %	*CaO %	K_2O %	Be ppm	Cu ppm	Ba ppm	Sr ppm	Zr ppm
52	0.05	.11	52.00	.01	.02	4.9	644	715	2
27	0.21	.17	48.20	.04	.02	6.5	106	489	7
29A	9.23	4.19	1.59	2.08	1.49	35.1	691	167	83
29B	5.26	2.59	1.15	1.30	1.08	46.7	455	107	53
31	3.83	2.00	0.30	.90	.79	20.8	435	78	32
32	3.56	2.32	0.28	.76	.32	16.6	524	90	23
33	2.16	2.01	1.03	.54	.77	6.4	356	47	21
34	4.45	1.71	.21	1.26	.99	9.1	614	80	34
35	9.59	4.22	1.31	2.09	1.50	34.7	767	196	83
36	2.61	1.78	.12	.51	.32	7.0	4830	76	22
37	6.92	2.97	.20	2.06	.30	20.6	457	70	53
38	3.10	20.90	.16	.82	1.37	57.1	254	51	39
39	2.52	17.90	.16	.71	.45	54.2	525	46	46
40	2.74	2.62	.37	.72	.50	11.2	382	33	33
41	5.39	2.55	.09	1.33	.48	7.9	511	67	37
42	2.28	1.50	.06	.71	.61	16.5	240	30	31
43	3.41	5.99	.06	.97	.51	40.3	369	29	47
44	4.51	5.36	.06	1.24	.54	11.3	319	41	56
45	2.13	28.90	.09	.58	.72	17.8	186	16	71
46	4.67	1.98	.07	2.22	.51	23.4	403	66	52
47	4.67	4.14	.07	1.36	.61	12.2	325	29	58
48	2.40	14.90	.21	.58	.30	48.1	351	37	41
50	7.50	3.39	.31	1.50	1.00	53.6	550	80	76
51	2.34	14.30	.05	.61	.59	15.6	251	16	55

* Total Fe expressed as Fe_2O_3

TABLE 7: Horse Canyon, X-Ray Diffraction Analyses
(analyses performed by the Saskatchewan Research Council).

	MINERAL CONTENT (Weight %)							
SAMPLE	Quartz	Calcite	Dolomite	Illite	Kaolinite	Chlorite	Smectite	Mixed Layer
27	10	81	8	0	0	0	0	0
37	84	5	0	10	0	0	0	0
42	95	0	0	5	0	0	0	0
45*	89	0	0	9	0	0	0	0
50	84	0	0	13	3	0	0	0

* sample 45 also contains 2% Hematite

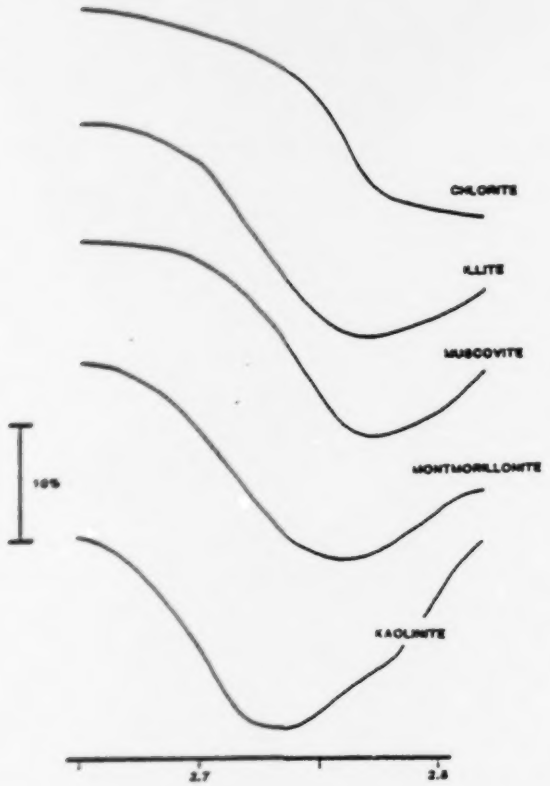

Figure 1: HHRR-Spectrometer Spectra of Selected Minerals in the Near Thermal Infrared (Half Bandpass 25 nm)

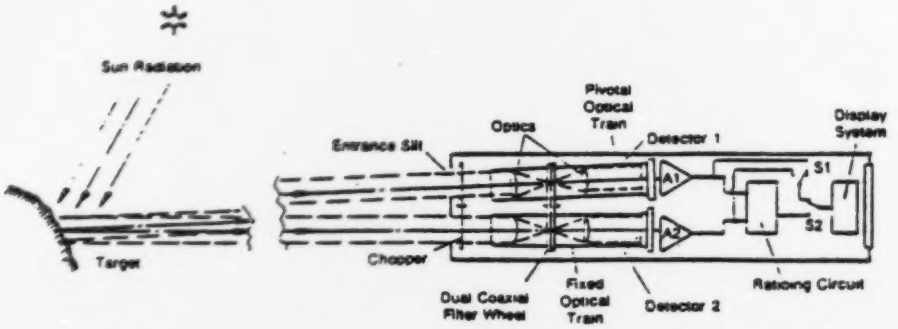

Figure 2: HHRR Simplified Schematic

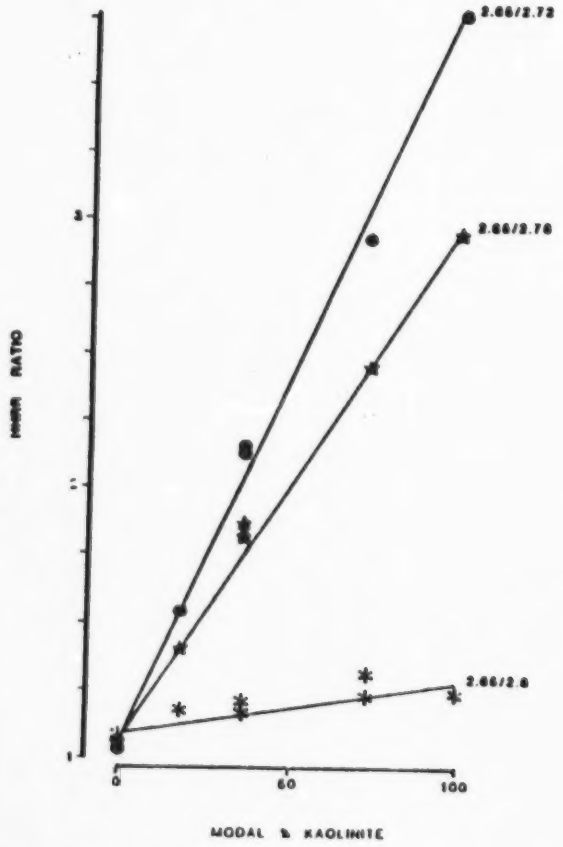

Figure 3: Kaolin Modal % Calibration Curves at Three Wavelengths (from Gladwell, 1982)

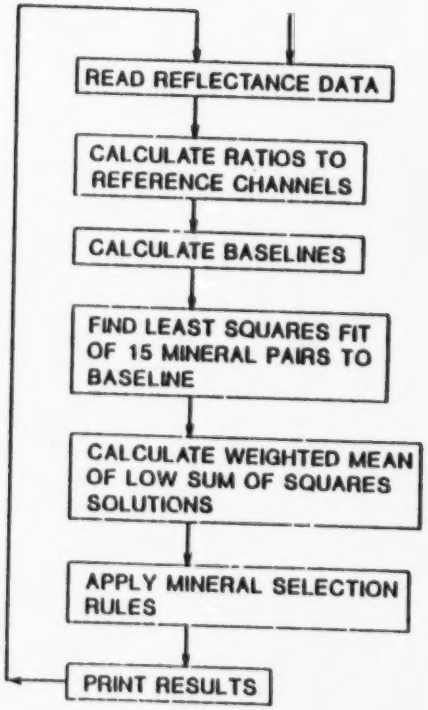

Figure 4: Simplified Flow Diagram of the Clay Mineral Analysis Algorithm

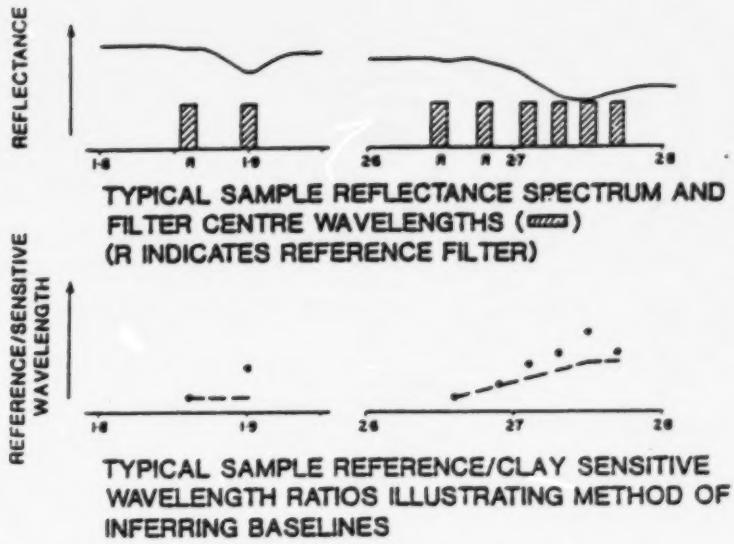

Figure 5: Typical Sample Reflectance Spectrum Showing Filter Positions and Method of Inferring Baseline when Alunite and Gypsum are not Present

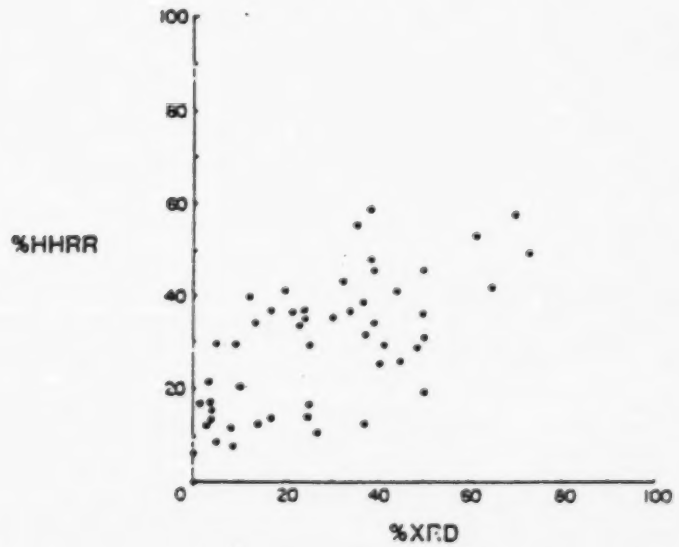

Figure 6: Comparison Between XRD and Reflectance Analyses of Illite, Illite/Smectite, Smectite and Muscovite Content of Test Sample Suite

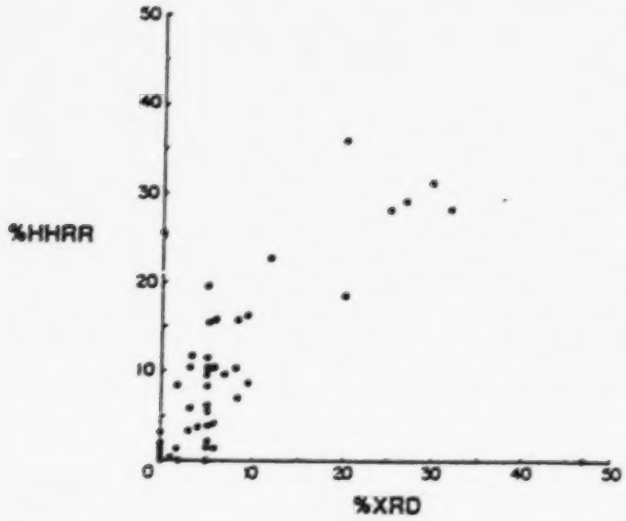

Figure 7: Comparison Between XRD and Reflectance Analyses
Kaolinite/Biotite Content of Test Sample Suite

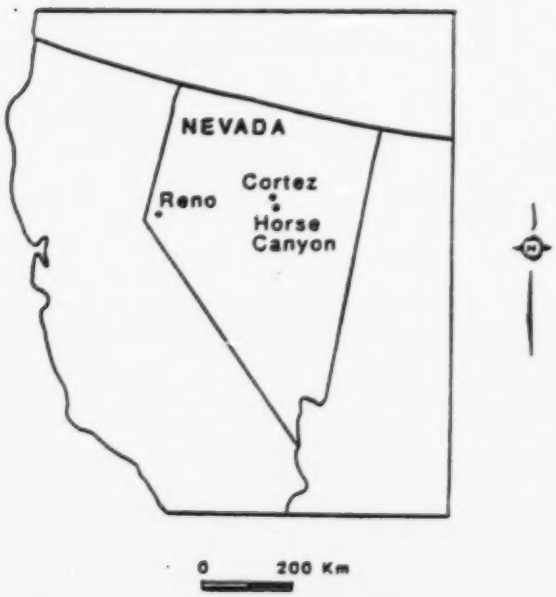

Figure 8: Horse Canyon Location Map

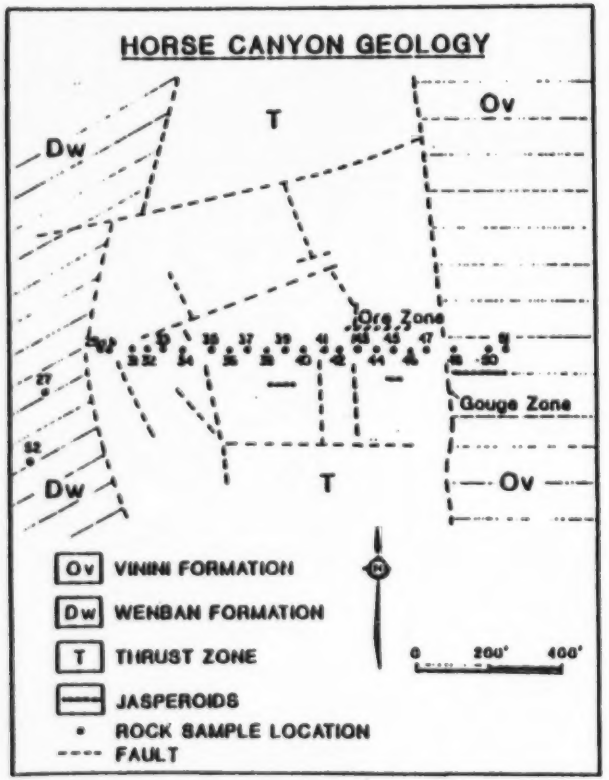

Figure 9: Horse Canyon Geology and Sample Locations

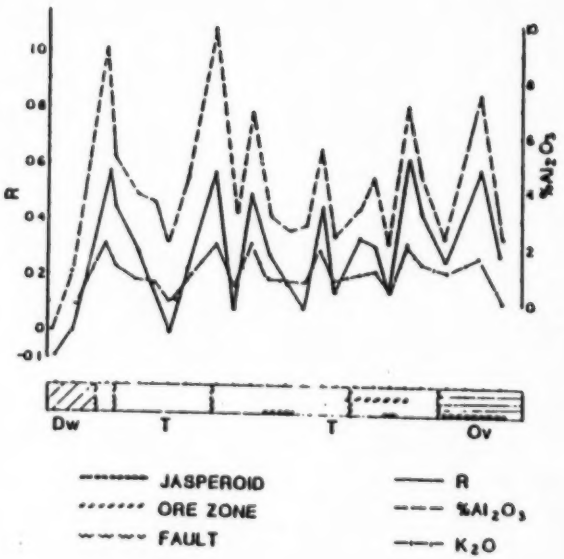

Figure 10: Horse Canyon, Comparison of the Reflectance Ratio 2.65/2.75 Micrometers (R) with Al_2O_3 and Geochemistry

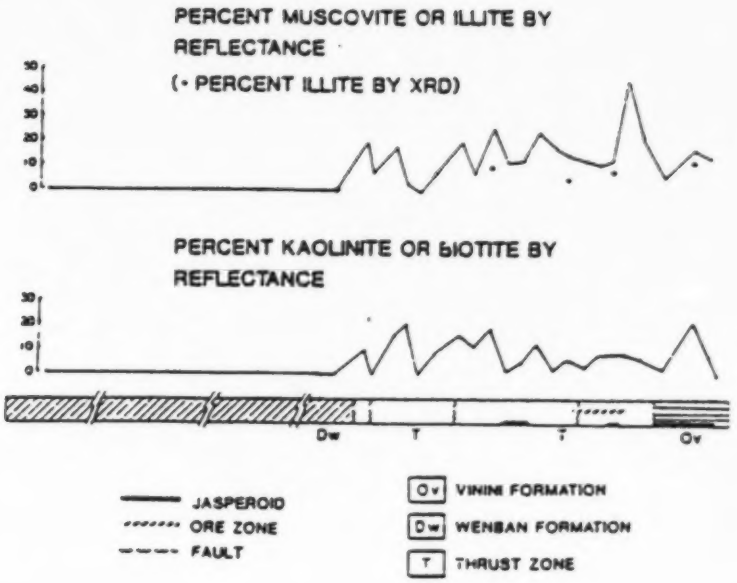

Figure 11: Horse Canyon, Distribution of Reflectance Determined Illite/Muscovite and Kaolinite/Biotite

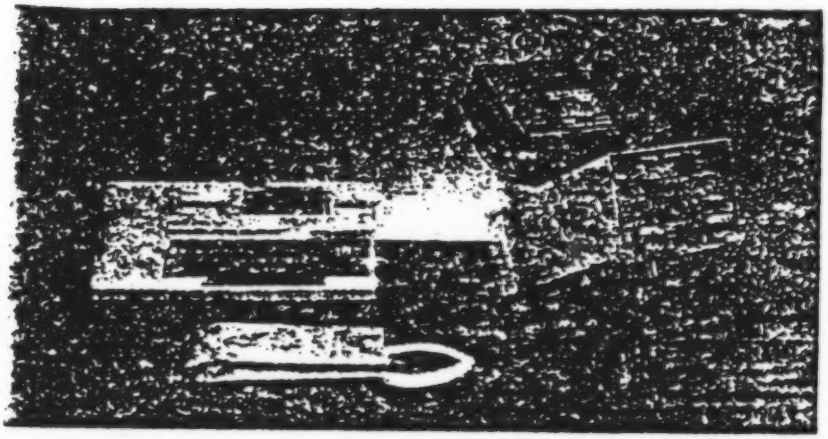

Figure 12: CLAYPAK, The Field Portable Clay Mineral Analysis System (cables omitted for clarity)